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THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

REPORT OF THE INTERNATIONAL COMMITTEE ON ATOMIC WEIGHTS.

Received November 3, 1903.

THE International Committee on Atomic Weights[1] has the honor to offer the following report:

In the table of atomic weights for 1904 only two changes from 1903 are recommended. The atomic weight of caesium has been slightly modified to accord with the recent determinations by Richards and Archibald, and that of cerium in conformity with the measurements by Brauner. The value for lanthanum is still in controversy, and any change here would therefore be premature. The same consideration may also be urged with regard to iodine. Ladenburg has shown that the accepted number for iodine is probably too low, but other investigations upon the subject are known to be in progress, and until they have been completed it would be unwise to propose any alteration.

Many of the atomic weights given in the table are well known to be more or less uncertain. This is especially true with respect to the rarer elements, such as gallium, indium, columbium, tantalum, etc. But some of the commoner elements also stand in

[1] The original members of the committee take great pleasure in announcing the addition to their number of Professor Henri Moissan. They are confident that this increase will meet with universal approval.

need of revision, and we venture to call attention to a few of these. Among the metals, the atomic weights of mercury, tin, bismuth and antimony should be redetermined, for the reason that the existing data are not sufficiently concordant. Palladium also, on account of discrepancies between different observers, and possibly vanadium, for which the data are too few, deserve attention. Among the non-metals, phosphorus has been peculiarly neglected; and our knowledge of the atomic weight of silicon rests upon a single ratio. In the latter case, confirmatory data are much to be desired. Upon any of these elements new investigations would be most serviceable.

There is one other point to which we may properly call attention. Many of the ratios from which atomic weights have been calculated, were measured in vessels of glass, by processes involving the use of strong acids. In such cases the solubility of the glass becomes an important consideration, even when no transfer of material from one vessel to another has occurred. A slight conversion of silicate into chloride would cause an increase of weight during the operation, and so introduce an error into the determination. Such errors are doubtless very small, and still they ought not to be neglected. Now that vessels of pure silica, the so-called quartz-glass, are available for use, they might well replace ordinary glass in all processes for the determination of atomic weights. An investigation into the relative availability of the two kinds of glass is most desirable.

(Signed) F. W. Clarke,
T. E. Thorpe,
Karl Seubert,
Henri Moissan,
Committee.

International Atomic Weights.

		O = 16.	H = 1.
Aluminum	Al	27.1	26.9
Antimony	Sb	120.2	119.3
Argon	A	39.9	39.6
Arsenic	As	75.0	74.4
Barium	Ba	137.4	136.4
Bismuth	Bi	208.5	206.9
Boron	B	11.	10.9
Bromine	Br	79.96	79.36
Cadmium	Cd	112.4	111.6
Caesium	Cs	132.9	131.9

		O = 16.	H = 1.
Calcium	Ca	40.1	39.8
Carbon	C	12.00	11.91
Cerium	Ce	140.25	139.2
Chlorine	Cl	35.45	35.18
Chromium	Cr	52.1	51.7
Cobalt	Co	59.0	58.56
Columbium	Cb	94.	93.3
Copper	Cu	63.6	63.1
Erbium	Er	166.	164.8
Fluorine	F	19.	18.9
Gadolinium	Gd	156.	155.
Gallium	Ga	70.	69.5
Germanium	Ge	72.5	71.9
Glucinum	Gl	9.1	9.03
Gold	Au	197.2	195.7
Helium	He	4.	4.
Hydrogen	H	1.008	1.000
Indium	In	114.	113.1
Iodine	I	126.85	125.90
Iridium	Ir	193.0	191.5
Iron	Fe	55.9	55.5
Krypton	Kr	81.8	81.2
Lanthanum	La	138.9	137.9
Lead	Pb	206.9	205.35
Lithium	Li	7.03	6.98
Magnesium	Mg	24.36	24.18
Manganese	Mn	55.0	54.6
Mercury	Hg	200.0	198.5
Molybdenum	Mo	96.0	95.3
Neodymium	Nd	143.6	142.5
Neon	Ne	20.	19.9
Nickel	Ni	58.7	58.3
Nitrogen	N	14.04	13.93
Osmium	Os	191.	189.6
Oxygen	O	16.00	15.88
Palladium	Pd	106.5	105.7
Phosphorus	P	31.0	30.77
Platinum	Pt	194.8	193.3
Potassium	K	39.15	38.86
Praseodymium	Pr	140.5	139.4
Radium	Ra	225.	223.3
Rhodium	Rh	103.0	102.2
Rubidium	Rb	85.4	84.8
Ruthenium	Ru	101.7	100.9
Samarium	Sm	150.	148.9
Scandium	Sc	44.1	43.8
Selenium	Se	79.2	78.6

Silicon	Si	28.4	28.2
Silver	Ag	107.93	107.12
Sodium	Na	23.05	22.88
Strontium	Sr	87.6	86.94
Sulphur	S	32.06	31.83
Tantalum	Ta	183.	181.6
Tellurium	Te	127.6	126.6
Terbium	Tb	160.	158.8
Thallium	Tl	204.1	202.6
Thorium	Th	232.5	230.8
Thulium	Tm	171.	169.7
Tin	Sn	119.0	118.1
Titanium	Ti	48.1	47.7
Tungsten	W	184.	182.6
Uranium	U	238.5	236.7
Vanadium	V	51.2	50.8
Xenon	Xe	128.	127.
Ytterbium	Yb	173.0	171.7
Yttrium	Yt	89.0	88.3
Zinc	Zn	65.4	64.9
Zirconium	Zr	90.6	89.9

THE VOLUMETRIC DETERMINATION OF ZINC.

By W. George Waring.

Received October 15, 1903.

The delicacy and precision of the ferrocyanide titration of zinc in properly conditioned solution is almost wholly negatived by inexact methods used for the separation of zinc from interfering elements and by misleading, contradictory and useless directions given in text-books.

An inquiry into the causes of extraordinary discrepancies in zinc determinations made by a number of public analysts, zinc works chemists, and college instructors upon identical samples has led the writer to prepare this paper, in which he endeavors first to discuss the sources of error peculiar to zinc determinations by the ferrocyanide volumetric methods, adding in the sequel, a description of the methods followed in his laboratory at Webb City, Mo., for the determination of zinc in various combinations.

SOURCES OF ERROR.

Losses may result from:

(1) Volatilization of zinc as chloride.

(2) Recombination of zinc with silica.

(3) Imperfect decomposition by acids.

(4) Occlusion by ferric hydroxide, etc.

(5) The use of hydrogen sulphide for separating copper, cadmium, etc.

(6) Failure to make the final titration under the same conditions as in standardization.

(7) Insufficient dilution of the solution.

(8) Too great haste in titrating, especially with cold solutions.

On the other hand, results may be too high, owing to:

(9) The presence, in the solution, of cadmium, copper, antimony, manganese, aluminum, or some organic acid as tartaric acid, oxalic acid, etc.

(10) The decomposition of the ferrocyanide solution by chlorine, bromine, nitrous oxides, hydrogen peroxide, etc.

(11) The addition of an inordinate excess of acid to the solution.

(12) The use of an incorrectly standardized solution of ferrocyanide.

(1) *Volatilization of Zinc Chloride.*—Although zinc chloride alone is volatile only at a red heat, it volatilizes freely at 145° C. and over when heated with ferric chloride and ammonium chloride, or with ammonium chloride alone, in an acid mixture such as often occurs in the course of the analysis of zinc ores. Experiments made to decide this point showed that when a solution of zinc and ammonium chloride in hydrochloric acid was evaporated to dryness, the mixture became pasty at 119° C., solidified at 120.5°, with a sudden decrease of the temperature to 117°, from which point the temperature rose rapidly, with evolution of aqueous vapors, to 145°, when the chloride began to sublime. A neutral solution of the same chlorides showed no volatilization of the chlorides up to 210°. When zinc blende, containing a little iron, was heated with aqua regia and evaporated with ammonium chloride, the mixture became pasty at 122.5°, solidified at 135°, with momentary recession of temperature to 132°, and volatilization of the chlorides began immediately after the temperature increased again, being very copious at 145°.

The evaporation of acid solutions containing zinc, iron and

ammonium chlorides should therefore not be finished at a temperature much exceeding 100°.

(2) *Recombination of Zinc with Silica.*—This invariably occurs when ammonia is added to a solution of zinc containing silica. The importance of removing silica by filtration before adding ammonia to separate iron, etc., has been demonstrated by Prost and Hassreidter,[1] as well as by other chemists; but this precaution seems to be disregarded in some American schemes, *e. g.*, the method of Von Schulz and Low. The following experimental results obtained in the analysis of ores containing silicate of zinc will illustrate this point:

(*a*) The first filtrate, without evaporating to separate silica, gave zinc 45.65 per cent. After dissolving out the ferric hydroxide from the silica on the filter by hydrochloric acid, precipitating iron, etc., by ammonia, and filtering through a clean filter, there was found 1.75 per cent. additional zinc in the filtrate. A repetition of the procedure gave 2.17 per cent. more zinc in the third filtrate. Total, 49.57 per cent.

(*b*) The same ore, decomposed as usual with hydrochloric acid, evaporation stopped very much short of dryness, water and ammonium chloride added, the gelatinous silica filtered off and washed, the iron precipitated by ammonia, dissolved and reprecipitated and the two filtrates titrated separately, gave, in first filtration, 49.15; in second, 0.50; total, 49.65 per cent.

(*c*) The same ore treated as in (*b*), except that the acid solution was evaporated to complete dryness at 180°, then taken up with water, filtered, and ammonium chloride and ammonia added. The first filtrate gave, as before, 49.15 zinc, and second, 0.50; total, 49.65 per cent.

The silica obtained in (*b*) amounted, after ignition, to 29.15 per cent. That from (*c*) to 29.50. Both (*b*) and (*c*) gave identical results for iron, namely, 1.43 per cent.

In the following cases, operating upon different ores, the silica was not removed until after the first precipitation by ammonia. Three precipitations were made in each case; the first and second filtrates titrated together and the third separately.

(*d*) Zinc in first and second filtrates, 36.35; in third, 6.60; total 42.95.

[1] *Ztschr. angew. Chem.* (1892), p. 168.

(*e*) Zinc in first and second filtrates, 35.80; in third, 7.00; total, 42.80.

(*f*) Zinc in first and second filtrates, 48.32; in third, 5.70; total, 54.02.

(3) *Imperfect Decomposition by Acids.*—Attention should be called to the insolubility of the zinc aluminates (the zinc spinels, Gahnite or Automolite and Dysluite found in the New Jersey ores, and the compounds formed in the zinc retorts). These are only perfectly decomposed by fusion with sodium or potassium bisulphate (see also page 25). Rhodonite and some garnets are said to contain zinc occasionally. We have never found any zinc in rhodonite, even in that from Broken Hill, Australia. Both garnet and rhodonite require fusion with alkaline carbonates.

(4) *Occlusion by Ferric Hydroxide, etc.*—It is stated by Sutton[1] that the iron precipitated by ammonia "tenaciously holds about one-fifth of its weight in zinc."

The following tables show the results of an examination as to the retention of zinc by ferric and aluminous hydroxides made in our laboratory some years ago. The method of analysis followed was the first one described in the sequel.[2] Variations are noted in or appended to the tables.

Table I.—Using pure materials containing known proportions of zinc and iron with no other substances which might affect the results.

No.	Zinc taken. Per cent.	Iron taken. Per cent.	Ammonium chloride added. Grams.	Water. cc.	Ammonium hydroxide. cc.	Zinc found in first filtrate.	Zinc found in second filtrate.	Total zinc found. Per cent.	Zinc retained by each part iron in first precipitate.
1	60	2	2	33	5	59.10	0.94	60.04	0.47
2	60	2	2	66	5	59.18	0.82	60.00	0.42
3*a*	60	2	2	132	5	59.02	1.03	60.05	0.51
3*b*	60	2	2	132	5	30.30	29.35	59.65	14.67
4	60	2	4	66	5	59.25	0.65	59.90	0.32
5	60	2	8	66	5	59.28	0.70	59.98	0.35
5*c*	60	2	8	66	8	59.48	0.42	59.90	0.21
6	60	10	4	66	5	58.80	1.50	60.30	0.15
7	60	10	4	66	10	58.87	1.23	60.10	0.12
8	60	10	6	66	10	58.90	1.00	59.90	0.10

[1] "Volumetric Analysis," 8th ed., p. 378.

[2] See page 20.

No 3*b* was evaporated to complete dryness and maintained at a temperature of about 120° for half an hour or more. The results in this case are instructive.

Table II.—Showing the proportion of the zinc retained by aluminum hydroxide, metallic aluminum being added to the assay instead of iron.

No.	Zinc taken. Per cent.	Aluminum taken. Per cent.	Equivalent to aluminum oxide.	Zinc found in first filtrate.	Zinc found in second filtrate.	Total zinc found. Per cent.	Parts zinc held by 1 part aluminum.	Ditto by 1 part aluminum oxide.
1	60	7.00	14.30	57.80	1.85	59.65	0.31	0.15
2	60	1.40	2.86	59.32	0.50	59.82	0.50	0.24

Table III.—Giving a few typical results selected from a large number of experiments made upon zinc blende concentrates, etc.

No.	Material.	Iron found. Per cent.	Zinc found in first filtrate.	Zinc found in second filtrate.	Total zinc found. Per cent.	Zinc retained by 1 part iron in first precipitate.
1	Pure yellow blende	0.33	65.30	0.26	65.56	0.79
2	"Sludge".....	1.12	57.37	0.60	57.97	0.54
16	Blende ore.....	3.54	49.92	0.55	50.47	0.31
19	Blende ore.....	4.95	53.77	1.11	54.88	0.22
20	Blende ore.....	5.86	48.90	1.00	49.90	0.17
21	Mexican blende...	13.54	42.90	1.50	44.40	0.11

In the four following, three precipitations of iron were made, each filtrate being titrated by itself.

TABLE IV.

No.	Material.	Iron found. Per cent.	Zinc found in first filtrate.	Zinc found in second filtrate.	Zinc found in third filtrate.	Total zinc found. Per cent.	Zinc to iron in second filtrate.	Zinc to iron in third filtrate.
1	Marmatite..	9.70	44.30	2.50	0.45	47.25	0.25	0.05
2	Blende.....	8.62	47.20	3.00	0.58	50.78	0.35	0.07
3	Blende.....	8.75	46.05	4.75	0.40	51.20	0.55	0.05
4	Blende.....	14.32	16.50	2.05	0.55	19.05	0.14	0.04

The following note, communicated by Geo. C. Stone, of the New Jersey Zinc Co., is of interest in connection with the separa-

tion of ferric iron by ammonia: "In the case of our ores we find that if a thoroughly oxidized solution is evaporated and heated to render the silica insoluble, treated with hydrochloric acid and washed, the resulting filtrate frequently contains some ferrous salt, making it necessary to oxidize before precipitating iron. I believe that the tendency of manganese salts to exert a reducing effect upon ferric iron in solution is probably the cause of this phenomenon. It certainly deserves investigation."

Manganese, when precipitated by oxidizing agents from solutions containing zinc, often carries down very considerable quantities of the latter, more especially when the precipitate contains lower oxides of manganese than manganese dioxide. In the presence, however, of considerable ferric iron, the manganese goes down as the black flocculent manganese hydroxide and little, if any, more zinc is carried down than would be the case if iron alone were present.

In the following experiments (Table V) the sample used contained a considerable proportion of willemite, together with franklinite and other minerals peculiar to the New Jersey ores. The silicious residue resulting from the treatment of the sample by hydrochloric acid, etc., was therefore separated by filtration before addition of ammonia. In No. 1 no ammonium chloride was added before the first precipitation by ammonia, but sufficient ammonium persulphate was added with the ammonia in each case to separate all the manganese as manganese hydroxide. In No. 2, four precipitations were made and the insoluble residue from the preliminary treatment was fused with potassium bisulphate to recover about 0.24 per cent. of zinc found to be insoluble, probably as dysluite. In No. 3 the sample was first treated according to Dr. Low's method,[1] and the first precipitate, including

[1] By Low's method is here meant the attack of the ore by a saturated solution of potassium chlorate in nitric acid, without previous decomposition by other means. An analysis of the same sample made by first decomposing the ore with strong hydrochloric acid, (franklinite is insoluble in the chlorate mixture) evaporating to dryness in a platinum dish, expelling silica by means of hydrofluoric acid, then treating the residue with the chlorate mixture, etc., gave a correct result with a single filtration. The separation of iron and manganese from zinc is absolutely perfect when the silica is first removed either by hydrofluoric acid or by Furman's more tedious but equally effective method, provided a diluent such as Dr. Low recommends is employed. Caution is required regarding the proper use of the chlorate mixture. If less chlorate is used than will precipitate all of the manganese, the results of the titration will be too high by 1.6 per cent. of zinc for every per cent. of manganese in the filtrate. If an excess of chlorate be used, and remain undecomposed, the titration will also give too high results, even when a large excess of sodium sulphite is added. This is due to a peculiar decomposition of the ferrocyanide that occurs when a chlorate is present in an acid solution.

the insoluble material, was redissolved and precipitated twice by persulphate and ammonia as in Nos. 1 and 2, giving two additional filtrates. An analysis of this sample made by the special hydrogen sulphide method described in the sequel gave:

Zinc	17.90	Aluminum oxide	2.00
Iron	20.35	Calcium oxide	10.93
Manganese	9.37	Insoluble	12.80

TABLE V.

No.	Manganese found. Per cent.	Iron found. Per cent.	Zinc found in first filtrate.	Zinc found in second filtrate.	Zinc found in third filtrate.	Zinc found in fourth filtrate.	Total zinc found. Per cent.
1	9.37	20.35	13.95	2.42	1.43	...	17.80
2	9.37	20.35	15.05	2.25	0.55	0.10	17.95
3	9.37	20.35	12.73	1.33	2.77	...	16.83

The sample used in the above tests is one of a set of three recently sent to a number of chemists as a preliminary to an inquiry into the causes of discrepancies in zinc analyses, instituted under the auspices of the Committee on Uniformity in Technical Analyses, New York Section of the Society of Chemical Industry.

To prevent manganic oxide from carrying down zinc when precipitated by bromine, peroxide of hydrogen, persulphate, etc., it appears to be absolutely necessary that the manganese shall be separated as hydrated binoxide, as before stated, and, if the separation is to be effected from an ammoniacal solution, it should be concentrated and contain a large amount of ammonium chloride. The recent researches of Dittrick and Hassel[2] on the separation of manganese by ammonium persulphate, in which it is found that manganese can be separated completely from zinc by having the solution highly diluted, refers to sulphuric acid solutions.[3] When no ferric compound exists in the solution, the persulphates give a brownish yellow slimy precipitate rich in zinc, but the addition of bromine water produces the black flocculent precipitate nearly free from zinc under the conditions prescribed. One part of ammonium persulphate precipitates about 0.6 part of manganese from an ammoniacal solution.

[1] *Ber. d. chem. Ges.*, **35**, 15, 3266-3271.

[2] See also papers on the subject by H. Baubigny, *Compt. Rend.*, **135**, 22, 965-967, and **136**, 7, 449-451.

Examples of occlusion of zinc by manganese:

(*a*) To a solution (from zinc ore) containing 0.262 gram of zinc, 0.0212 gram of iron and 0.1043 gram of manganese in 35 cc., there was added 3.5 grams of ammonium chloride, 0.5 gram of ammonium persulphate and 7 cc. of ammonia; the solution was boiled, filtered and washed. The precipitate contained 0.01375 gram of zinc.

(*b*) A solution of the same volume containing the same amounts of zinc and iron, but no manganese, treated exactly like the foregoing, gave a precipitate containing 0.0033 gram of zinc.

(*c*) A repetition of the first experiment, using 150 cc. of water, instead of 35, gave a precipitate containing 0.0295 gram of zinc.

The following results of the precipitation of manganese by bromine from acetate solutions containing, in each case, 0.2265 gram of zinc and 0.2609 gram of manganese, have been communicated to me by Mr. Geo. C. Stone: "The manganese found was 0.3045, 0.2945, 0.2895, 0.2840, and 0.2864; in the sixth the manganese was not weighed. The zinc found in the same solutions was 0.1763, in the second it was not weighed, 0.1860, 0.1780, 0.1858 and 0.1795. As you will see, with a large proportion of manganese the error is a serious one."

The well-known method of separating manganese from iron and zinc by means of nitric acid and potassium chlorate does not appear to give satisfactory results in many cases. In our laboratory, recourse is now had to a separation of the zinc as sulphide for all control or umpire work upon material containing manganese and other interfering elements.

Calcium fluoride, which frequently occurs in zinc ores, does not appear to occlude zinc in the ordinary ammoniacal precipitate. Thus a crude ore from Illinois containing 24.24 per cent. of zinc as sulphide, 0.44 per cent. of iron, 31.37 per cent. of calcium carbonate, and 17.96 per cent. of calcium fluoride, gave 24.05 per cent. of zinc in the first filtrate and 0.25 per cent. in the second, with quite sharp end-reactions. An analysis in which the zinc was separated as sulphide gave 24.25 per cent. of zinc.

(5) *The Use of Hydrogen Sulphide for Separating Cadmium, etc.*—The inexactitude of this process may be inferred from the classic experiments of Fresenius, but in view of Dr. Low's advocacy of its use in technical analysis, it seemed advisable to

make some additional tests, following his directions precisely. These tests fully confirmed the statements of Fresenius, showing that it is impossible to separate even a small proportion of the cadmium without at the same time separating a very considerable proportion of the zinc.

Although it appears to be impracticable to separate cadmium completely from zinc by hydrogen sulphide, yet if the acidity of the solution is reduced so as to allow a complete precipitation of the cadmium along with nearly all the zinc, and the precipitate is afterwards treated with dilute hydrochloric or sulphuric acid, containing about 5.5 per cent. of absolute hydrochloric acid or 8 per cent. sulphuric acid, without heating, but with vigorous stirring or agitation, the zinc goes into solution while the excess of hydrogen sulphide, set free in the liquid, prevents any of the cadmium from dissolving. The development of the pure, bright yellow color of cadmium sulphide affords a visible means of controlling the operation with hydrogen sulphide water, if necessary. The detection and estimation of cadmium with accuracy, although not essential for most technical purposes, is, in some cases, *e. g.*, in oxide manufacture, of very great importance.

Items 6, 7 and 8 require only the following explanatory remarks: The brown-red color of uranyl ferrocyanide is more or less discharged by moderately strong acid, so that only the excess required to promote the formation of the insoluble double ferrocyanide of potassium and zinc should be present, and the amount of this excess must be the same in standardization as in titrating. If the amount of zinc present greatly exceeds 0.1 gram to 100 cc., some zinc chloride or normal ferrocyanide appears to be enclosed in the precipitate so that a low result ensues. Heat, as well as the presence of hydrochloric acid and ammonium chloride, promotes the transformation of the normal ferrocyanide into the insoluble double ferrocyanide. The completion of this reaction is extremely slow in cold solutions. Under the next item (9) attention will be drawn to a similar but much more pronounced delaying of the end-reaction due to the presence of cadmium.

(9) *Plus Errors Due to the Presence of Copper, Cadmium, Antimony, Manganese, Aluminum, Organic Acids, etc.*—In technical work the slightly higher results due to mere traces of such elements are disregarded, but when extreme accuracy is required, the cumulative effect of minute amounts of other metals must be

duly considered. Thus the presence of 0.06 per cent. of copper in a zinc blende gives no indication of its presence in an ammoniacal solution of 200 cc., yet it increases the zinc result by a little over 0.1 per cent. by actual test.

The erroneous statements found in various publications regarding the compounds formed when ferrocyanide is added to the solution of a cadmium salt have been made the subject of some research by the writer.

The research confirmed the results obtained by Dr. E. H. Miller,[1] which led him to conclude that the precipitates obtained under different conditions could be resolved into mixtures of two simple ferrocyanides: Cd_2FeCy_6 in which 3Zn equals 4Cd, and the zinc factor multiplied by 2.291 equals the factor of cadmium, and $K_2CdFeCy_6$ in which 3Zn equals 2Cd and the cadmium factor is 1.1454 times the zinc factor.

It also developed a peculiar reaction due to the presence of ammonium chloride, which led to the discovery of what is believed to be a new ferrocyanide of ammonium and cadmium.

When a quite acid solution containing cadmium, but no ammonium salt is titrated with ferrocyanide until the color reaction appears with uranium, and ammonium chloride is then added, the color reaction disappears and does not reappear until after a very considerable further addition of ferrocyanide. The ferrocyanide actually used corresponds to a factor ratio of zinc to cadmium as 1.0 to 1.245 and 1.0 to 1.243 upon duplicate trials. Th precipitate, when dried, was analyzed by distillation with caustic soda and found to contain Cd 32.62 per cent., NH_4 11.30 per cent., $FeCy_6$ 56.08 per cent., giving approximately the empirical formula $(NH_4)_2CdFeCy_6$. It is of a light bluish color when dry, is anhydrous and appears to be quite insoluble in hydrochloric acid.

Under the conditions existing in a zinc analysis, namely, the presence of about 4 per cent. by measure of strong hydrochloric acid and 3 per cent., or more, of ammonium chloride, if as much as 0.002 to 0.003 gram of cadmium and 0.2 to 0.3 gram of zinc are present in about 250 cc. of solution, the presence of the cadmium is shown at the end of the titration by the fading of the first faint coloration in the testing drops, which fading will extend to 2 or 3 drops, or proportionately more with larger amounts of

[1] This Journal, **22**, 541, and **24**, 226.

cadmium. A permanent end-reaction is obtained when about as much ferrocyanide has been consumed for each part by weight of cadmium as would be required for 0.62 part of zinc. This ratio corresponds with no definite compound of ferrocyanogen and cadmium, and varies with the conditions of the analysis. The accurate determination of zinc in the presence of cadmium, or of cadmium, either alone or in the presence of zinc, is therefore impossible by means of ferrocyanide.

Fortunately, however, we have in metallic aluminum[2] a means of quickly and completely separating cadmium, as well as the other metals of the lead group, from zinc by boiling in a moderately acid solution, from which the zinc can be precipitated by hydrogen sulphide after filtration and neutralization.

The effect of aluminum salts on the titration of zinc has been shown by Miller and Hall[2] to yield irregular results. We have found that 200 cc. of a solution containing 0.3032 gram of zinc and 0.299 gram of aluminum, both as chlorides, with the usual amounts of free hydrochloric acid and ammonium chloride, required 63.40 cc. of ferrocyanide instead of 61.22 cc., which would have been sufficient in the absence of aluminum.

Oxalic acid increases the amount of ferrocyanide required. Thus in five cases where lime had been separated as oxalate from a strongly ammoniacal zinc solution, the acidified filtrates required respectively 0.97, 0.40, 1.00, 0.35 and 0.65 cc. more than would have been required in the absence of oxalic acid.

(10) *The Decomposition of Ferrocyanide by Oxidizing Agents* Cl, Br, H_2O_2, N_2O_3, etc.).—When these are used for separating manganese, the usual procedure is to destroy the excess by means of a sulphite. We find it advantageous to use sodium sulphite in making up the ferrocyanide solution, thereby obtaining the additional advantage of rendering the latter quite permanent. Chlorates must be completely decomposed before titration, as they seriously affect the result even in the presence of sulphites (see footnote, page 9).

(11) *The Use of Too Much Hydrochloric Acid.*[3]—We found that 0.233 gram of zinc with 4 grams of ammonium chloride in

[1] If cadmium is to be precipitated by aluminum, the solution must be rather strongly acid and must be boiled or the precipitation will be very slow. If copper is to be precipitated, the solution must be free from ammonium salts.

[2] Miller and Hall: *School of Mines Quart.*, **21**, 270.

[3] Miller and Hall: *Loc. cit. ante.*

8 cc. of hydrochloric acid and 250 cc. of water required 47.30 cc. of ferrocyanide, while with 15 cc. additional of hydrochloric acid the same amount of zinc required 47.55 cc.

(12) *The Use of an Incorrect Standard.*—The value of 1 cc. of the ferrocyanide is usually determined by titrating the solution of a weighed amount of calcined zinc oxide, or, supposedly pure metallic zinc.[1] The stick zinc made by Merck and Schuchardt is almost absolutely pure when fresh, but soon acquires a coating of oxide which seriously diminishes its value.

A special grade of so-called "C. P." zinc in sheets has recently been place on the market, for use in standardizing. It is very convenient because its thickness is such that one square centimeter weighs almost exactly 0.1 gram (0.101 gram) and contains very nearly 0.1 gram of zinc. An analysis of a bright, but unwashed sample gave: Zinc, 98.86; lead, 1.09; iron, 0.02; oxygen, 0.03.

The actual value of any sample of fairly pure sheet zinc, if it contains no cadmium, can be accurately determined by standardizing against pure zinc by titration with ferrocyanide. In this way it is found that many of the expensive forms of zinc sold by the chemical dealers are in reality no purer than, and in some cases not as pure as, some of the high-grade spelters.

Some of the zinc oxides sold as "C. P." are also very impure. We find, however, that several of the German makes, when obtained in the original packages, contain no appreciable impurities, and, after calcination in a platinum dish in a perfectly clean, new muffle and cooling over sulphuric acid, can be kept for months in a tightly stoppered bottle without change.

A number of experiments were made to determine the rate at which zinc oxide gained or lost water and carbonic acid when exposed under different conditions, but the results varied so greatly for different samples exposed at the same time that the results were of no value.

At a meeting of chemists held in Joplin, Mo., in 1900, a proposal was made to test the stability of pure natural blende in fine powder, with a view to its use for standardizing.

Ten grams of a special sample, found by concordant analyses

[1] Metallic zinc for standardizing should be digested with ammonia and ammonium chloride, then washed thoroughly, first with water, then with pure alcohol and well dried. It will then keep for many weeks without sensible change, if not exposed to moisture or acid vapors.

by chemists in Europe and America to contain 65.51 per cent. of zinc, gained 0.004 gram in weight after exposure for two days over water charged with carbonic acid. After twelve hours' exposure over dilute hydrochloric acid it gained 0.0735 gram additional, after forty-eight hours 0.0985 gram, and after twenty days 1.0705 grams. Six days' desiccation over sulphuric acid reduced the total gain to 0.2590 gram. 5.32 grams of the original sample exposed, in a muffle, to a temperature of 400° for 45 minutes, lost 0.0304 gram in weight.

ANALYSES OF BLENDES.

The following analyses were made with the utmost care, using 5 to 10 grams of ore for the determination of the metals other than zinc, and are representative. They were not made in the ordinary course of commercial work, but especially to accompany this paper.

Ore.	Zinc.	Iron.	Lead.	Copper.	Cadmium.
Sphinx Mine, Neck City, Mo.....	65.77	0.55	0.00	0.077	0.135
Ore from Golconda, Ill	60.55	1.18	0.51	0.046	0.110
Average of 2270 car-loads from Webb City, Mo.....	57.08	2.60	0.90	0.050	0.337
Standard Mine, Fortuna, Mo.....	61.97	0.55	0.815	0.133	0.436
Maude B. Mine, Webb City, Mo....	55.70	4.90	trace	trace	0.227
Big Six Mine, Aurora, Mo.....	56.75	1.88	none	0 004	0.018
McKinley Mine, Prosperity, Mo....	57.20	1.25	5.29	none	0.550
Hudson Mine, Pleasant Valley, Mo.	62.05	0.61	none	0.030	0.322
Big Circle Mine, Oronogo, Mo.....	56.90	1.64	1.51	trace	0.110
Willard Mine, Mo.....	63.30	0.80	0.41	0.064	0.320
Gundling and Standard, Fortuna, Mo.	63.50	0.90	0.32	0.107	0.530
October Mine, Webb City, Mo.....	58.10	2.74	0.59	none	0.460
Majestic Mine, Webb City, Mo.....	57.05	1.82	1.61	none	0.330
Three Shaft, Carterville, Mo.....	60.20	2.08	0.89	0.090	0.140
Uncle Sam Mine, Aurora, Mo.....	61.20	0.75	none	0.010	0.590
Crittenden Co. ore, Kentucky.....	53.58	0.77	0.76	none	0.211
Underwriters Mine, Webb City, Mo.	57.95	1.60	1.62	....	0.710
Jack Rose Mine, Joplin, Mo.....	54.70	1.36	1.02	....	0.260
Blende from Kentucky Fluorspar Mines.....	53.50	0.77	0.76	none	0.211
Average of 2145 shipments, Joplin District.....	57.75	2.32	1.07	0.042	0.388

I desire here to express my obligations to Mr. Geo. C. Stone, of the New Jersey Zinc Co., Mr. C. V. Petraeus, of the Lanyon Zinc Co., and Dr. Edmund H. Miller, of Columbia University,

for valuable suggestions and assistance rendered in the preparation of this paper.

I append a description of the methods of analysis employed in our laboratory for the technical estimation of zinc.

THE VOLUMETRIC DETERMINATION OF ZINC AS PRACTICED IN THE LABORATORY OF WARING AND SON, WEBB CITY, MO.

(A) *Stock Solutions.*

(1) *Standard Potassium Ferrocyanide.*—21.63 grams of Merck's pure potassium ferrocyanide and 7 grams of sodium sulphite crystals are dissolved in pure, non-aërated distilled water, the solution made up to exactly 1 liter and thoroughly mixed. Usually 10 liters of solution are made at a time and kept in a 3-gallon demijohn from which it is siphoned to the burette as required. Theoretically, 21.544 grams of ferrocyanide is required per liter, but, owing to impurities in the so-called "C. P." salt, we find that from 21.55 to 21.80 grams are necessary. One cc. of this solution should be equivalent to 0.005 gram of zinc.

(2) *Standard Zinc Acetate.*—6.23 grams of pure, freshly ignited zinc oxide are dissolved in 60 cc. of 30 per cent. acetic acid with the aid of heat and, when perfectly cold, made up to exactly 1 liter. One cc. contains 0.005 gram of zinc. The acetate is much the most satisfactory salt of zinc for this purpose, though the sulphate or chloride can be used. The chloride causes the burette cock to stick, while the acetate is a lubricator.

(3) *Uranium Acetate (Indicator).*—Dissolve 4.4 grams of the pure salt[1] (Merck's or Schuchardt's) in 100 cc. of distilled water and 2 cc. of acetic acid. This amount is sufficient for 200 zinc determinations. If a pure acetate is not available, use the nitrate, 52 grams to the liter.

(4) *Standard Potassium Permanganate.*—Exactly 20.1 grams of the pure salt are dissolved and the solution made up to exactly 7 liters with pure aërated distilled water. One cc. of this solution should be equivalent to 0.005 gram of iron or 0.0025 gram of lime.

(5) *Stock Solution of Ammonium Chloride.*—200 grams of pure ammonium chloride are dissolved in a liter of distilled water

[1] The label "Uranium Acetate, Merck, highest purity," does not necessarily mean pure uranyl acetate, as the sodium uranyl acetate is so designated as well as the sodium-free salt. See *Proceedings Missouri Pharmaceutical Association*, 1903, pp 23-37.

and 10 cc. of ammonia. For use 30 to 50 cc. of this solution are added to a liter of water in a wash-bottle.

(6) *Dilute Hydrochloric Acid.*—One volume of the strong acid (sp. gr. 1.20) is mixed with three volumes of distilled water; used in a wash-bottle.

(7) *Dilute Sulphuric Acid.*—One volume of strictly pure strong acid is poured slowly, with constant stirring, into three or four volumes of distilled water and, when perfectly cold, made up to five volumes.

(B) *Standardizing.*

(1) *The Ferrocyanide Solution.*—Weigh out, as nearly as practicable, 0.3 gram of Merck's or Schuchardt's "C. P." zinc,[1] or exactly 0.37338 gram of "C. P." freshly ignited zinc oxide (equal to 0.3 gram of zinc), and dissolve in 25 cc. of the dilute hydrochloric acid, add 3 to 4 grams of pure ammonium chloride and dilute to 200 cc. with distilled water at about 60° C. Titrate at once with the ferrocyanide solution, running in about 58 cc. at once with vigorous stirring. Note the change at this point in the appearance of the precipitate, a change from bluish white, thickish skim milk, to nearly pure white, accompanied by a thinning of the solution and a separation of the $K_2Zn_3(FeCy_6)_2$ in flocculent form on standing for a minute, especially if the stirring has been vigorous. This appearance always occurs, at a temperature of about 60°, when the titration is within 2 or 3 cc. of completion. Run in 2 cc. more and the precipitate will lose its flocculent appearance and will remain suspended for a considerable time. Test two or three drops of the solution by running them off the end of the stirring rod on to a drop of the uranium solution placed on a perfectly clean white porcelain plate. The solution must be *thoroughly* stirred each time and the rod and sides of the precipitating vessel be washed with a jet of hot water, after each addition of ferrocyanide, before testing. The test should give no tinge of brown or even the slightest flash of discoloration. Run in the ferrocyanide now drop by drop, testing after each addition, until a distinct, though faint, flash of color is observed. When a definite reaction is obtained, allow the color to develop, which will require from two to three minutes. Frequently it will be seen that, in addition to the drop which first gave the reaction, from

[1] See note, p. 15.

one to five of the others develop a brown-red color. If this be the case, deduct from the burette-reading the fraction of a cubic centimeter corresponding to the number of drops that show a color, in order to obtain the correct reading. The dilution coëfficient, *i. e.,* the amount of ferrocyanide necessary to give a reaction with uranium in a solution of the temperature and volume and containing the amounts of free acid and ammonium chloride that are in the solution being tested, at the end of the titration, is usually about 0.35 cc. and must always be deducted from the burette-reading. The standardization should always be made in duplicate or triplicate.

If the solution is found to be exactly standard, or within 0.25 cc. of the standard, it will only be necessary, when 0.5 gram of ore is taken for analysis, to deduct the dilution coëfficient from the burette-reading in order to obtain the percentage of zinc in the ore. If the variation from the standard is greater than 0.25 cc., divide the number of milligrams of zinc used for standardizing by five times the burette-reading (less the dilution coëfficient). To obtain the percentage of zinc in an analysis, the net burette-reading is to be multiplied by this factor, which should vary but little from unity.

The reactions between zinc chloride and potassium ferrocyanide occur as follows: At first the normal zinc ferrocyanide is formed; thus,

$$4ZnCl_2 + 2K_4FeCy_6 = 8KCl + 2Zn_2FeCy_6,$$

when about 45.5 cc. of the standard ferrocyanide solution has been added to a chloride solution containing 0.3 gram of zinc. If the temperature is low (20° to 25°), it will be found that a yellowish brown coloration is produced with uranium on the addition of more ferrocyanide. This coloration (which does not appear with hot solutions) will, however, fade gradually, but it will be yielded by the solution up to, nearly, the point at which the precipitate becomes flocculent, when it wholly disappears. The final, and permanent, coloration occurs when the following secondary reaction has been completed, as shown by Konick and Prost:[1]

$$6Zn_2FeCy_6 + 2K_4FeCy_6 = 4K_2Zn_3(FeCy_6)_2$$

whence $3Zn\ (196.23) : 2K_4FeCy_6,3H_2O\ (845.50) :: 5 : 21.5436.$

[1] *Ztschr. angew. Chem.* (1896), pp. 460–461.

After a little experience, the coloration produced after the first reaction causes no difficulty, even with a cool solution, since the color is different and fades on standing instead of becoming more intense, and the solution retains the bluish skim-milk color which differs from the pure creamy white of the later reaction.

The presence of a trace of copper in the solution also affords an indication of the passing of the three-quarter point. The normal ferrocyanide of copper gives a light chocolate tint to the solution, if present in the merest traces in a zinc solution, but when the three-quarter point is passed the chocolate tint changes to a blue, which does not interfere with the final reaction. The presence of copper increases the apparent result by about 1.8 parts zinc for each part of copper.

(2) *Permanganate.*—This solution is standardized by means of ferrous ammonium sulphate as directed by Fresenius' and other handbooks. It is advisable to add a piece of pure zinc before solution of the ammonium salt, and a little acid, then when the solution is complete and cooled, to decant and wash before titration.

THE ZINC ANALYSIS.

The simple analysis, applicable to pure carbonate and blende ores, will be given first; then the modifications applicable to:

(*a*) Silicates and calcined ores.

(*b*) Impure zinciferous ores containing considerable zinc, with copper, cadmium, manganese, antimony, silver and other elements.

(*c*) Low-grade zinc ores, slags, furnace residues, etc.

In the case of pure blende or carbonate ore containing only zinc, lead, iron and rock, it is usual to take 0.5 gram of the finely ground and dried sample for analysis. With low-grade material, larger amounts should be used so that the quantity taken for the analysis should contain approximately 0.2 to 0.3 gram of metallic zinc.

Transfer the weighed ore carefully and completely to a flat-bottomed flask of 150 to 250 cc. capacity—the so-called "copper determination flasks" made by Whitall Tatum Company are excellent for this purpose, as are also small Erlenmeyer flasks. Add about 4 cc. each of strong nitric and hydrochloric acids, washing down with the acid any part of the ore that may have adhered to the neck of the flask, set it on the hot plate in the fume chamber and

boil until red fumes are no longer evolved. Add about 3.5 grams of granular ammonium chloride and continue boiling until the contents of the flask intumesce, becoming thick and pasty, avoiding too great a heat as the volatilization of the ammonium chloride with white fumes must be prevented. While the mass is still moist, but so nearly dry that it has stopped intumescing, remove it from the heat, add about 30 cc. of hot water, twirl the flask a few times to cause all the soluble matter to dissolve,[1] add 6 to 7 cc. of strong ammonia, boil for a minute, filter and wash out the flask four times with hot dilute ammonia and wash the precipitate, on the filter, four times more with the same solution. The washed ferric hydroxide always contains a considerable amount of zinc which cannot be removed by washing, so that it is necessary to dissolve and reprecipitate the iron. Set the funnel and precipitate in the neck of the flask in which the ore was dissolved, dissolve the precipitate by means of a spray of hot, dilute hydrochloric acid, using no more acid than is necessary; from 6 to 10 cc. should be enough. Place about 0.5 gram of ammonium chloride in the filter and wash three times with hot water and then once with dilute ammonia. Reject the insoluble residue. Add about 4 cc. of ammonia to the solution, boil, filter and wash as before.

Both of the ammoniacal filtrates containing the zinc should be perfectly colorless; if a blue tinge is perceptible, copper is present and must be removed as directed under modification (*a*). If no copper is present, add 15 cc. of strong hydrochloric acid, warm the solution to 50° or 60° and transfer it to a precipitating-jar of moderately thick glass. Titrate with ferrocyanide, adding at once within 10 or 15 cc. of the amount judged to be necessary. Note the appearance of the liquid as to the bluish skim-milk complexion, add 3 or 4 cc. at a time, stirring very thoroughly each time until the precipitate becomes flocculent, then less and less until the opaque, white, non-flocculent characteristic appears, then add 3 to 5 drops at a time, testing with uranium after each addition. When only from 2 to 5 drops of ferrocyanide are required to complete the precipitation, an experienced eye will detect a peculiar darkening of the test, not, however, showing any tinge

[1] If the appearance of the undissolved residue indicates the presence of gelatinous silica, the contents of the flask must be filtered into another flask and washed six or seven times with hot water, before adding ammonia (see remarks under modification (*a*)).

of color, so that the final reaction may be reached by means of single drops of the precipitant. For a beginner, it is best to reach a decided color reaction by means of 0.5 cc. additions and drop-tests, and then titrate back with standard zinc acetate solution added by single drops, testing after each drop. This must be continued until at least three or four drops have been tested without showing the faintest tinge of brown coloration, and then two or three minutes' time, at least, be allowed for the color to develop in the drop that marks the exact end-point. It will be noticed that when nearing the precise end of the reaction, a momentary darkening of the drop, as before stated exceedingly faint, will appear when the drops of zinc solution come in contact with the uranium acetate drop, immediately disappearing as the drops become mixed, so that for a minute or so the mixture is pure white, then the faint brown color begins to appear and grow darker until a distinct red-brown color is finally established. When the end-point is passed, no trace of momentary tint shows at the contact. The color reaction in this test, although requiring time to develop, is exceeding delicate and definite, and, with proper care in the preparation of the solution, duplicate and triplicate determinations will agree to a single drop, that is, to within 0.05 per cent. It is important that the volume of the solution to be titrated should be nearly 75 to 100 cc. for each 0.1 gram of zinc present. The sharpness of the end-reaction depends also in a great measure on the percentage of free hydrochloric acid in the solution; it should always be at least 3 per cent. by volume, of strong acid (sp. gr. 1.20).

Modification (a). For Ores Containing Soluble Silicates.— When soluble silicates are present in an ore, the method described above fails because a considerable portion of the zinc is precipitated as silicate when ammonia is added to an acid solution containing soluble or gelatinous silica; several solutions and reprecipitations will not bring all the zinc into solution unless the silica is first removed by filtration.

In the presence of soluble silicates, the following method gives satsfactory results. The weighed sample of pulverized ore is placed in a porclain casserole, moistened with a few drops of water and spread over the entire bottom with a stirring rod; a mixture of 1 cc. of nitric and 6 cc. of hydrochloric acid is added and the ore stirred, to prevent clotting, until complete gelatiniza-

tion has taken place. Evaporate gently, after stirring in 3 to 4 grams of ammonium chloride, until the mass is nearly dry, *i. e.*, until it is no longer quite wet, but will crumble on stirring. It is not necessary to carry the evaporation to complete dryness, nor is it advisable. Dilute with hot water, filter and wash seven times with hot water, catching the filtrate and washings in a 250 cc. flask. A little experience will enable one to stop the evaporation at the point where the gelatinous silica can be most rapidly filtered and washed; at this point not more than 0.005 gram of silica will remain in solution. The filtrate is now ready to be precipitated with ammonia and treated as already described. Should the ore contain manganese, it must be removed as described in the next section, before precipitating with ammonia.

Modification (*b*). *For Impure Ores Containing Zinc with Either Manganese, Copper or Cadmium, or All of These Metals with Other Elements.*—In the absence of cadmium, or when it is not to be estimated, the ore is to be decomposed as first described, or as in (*b*), if soluble silicates are present, increasing the proportion of nitric acid, if considerable sulphides are present. After the zinc is dissolved and the ammonium chloride added, add 0.03 gram of ammonium persulphate and 10 cc. of bromine water for each 0.01 gram manganese possibly contained in the solution, then 7 cc. of strong ammonia, and boil for two or three minutes before filtering. The manganese will be precipitated as hydrated binoxide along with the ferric hydroxide. When but little manganese is present, it is not necessary to redissolve the manganese hydroxide to obtain the whole of the zinc. If the precipitate is broken up by a jet of warm, dilute sulphuric acid, only the iron and zinc will be dissolved, so that only a small amount of sodium persulphate and bromine need be added before the second precipitation. When but little iron is present, it is well to dissolve by hot dilute hydrochloric acid, allowing, as before, what manganese hydroxide fails to go into solution to remain on the filter. When bromine is used as an oxidizing agent, any excess will show its presence by an orange or orange-red color when the solution is acidulated before titration. Any free bromine present must be removed by the addition of sodium sulphite or it will oxidize the first portion of ferrocyanide added in titration.

When the ore contains copper, the blue ammoniacal zinc solu-

tion should be neutralized by hydrochloric acid and an excess of 5 cc. added, then a gram or two, or even more, if much copper is present, of very fine, pure "Freiburg" test lead and the solution boiled for ten to twenty minutes, by which time all the copper will have been precipitated on the lead. When cool enough, the solution is decanted into the precipitating-jar, 8 cc. more hydrochloric acid added, and the titration for zinc proceeded with. The lead in the acid solution does not interfere in the slightest degree with the zinc determination. On the addition of ferrocyanide a chocolate-brown tint appears, if the copper was not completely separated. This color changes to a fine cobalt-blue towards the end of the titration, at which point the blue tint sometimes disappears altogether.

When cadmium is to be separated as well as copper, it is customary, in many laboratories, to evaporate the acid sulphate solution of the ore (without the addition of ammonium chloride or nitrate) to dense white fumes, cool, digest with water to dissolve basic sulphates, filter out lead sulphate and insoluble matter, dilute until the proportion of free sulphuric acid is less than 8 per cent., then to heat and pass hydrogen sulphide until all the cadmium and copper and, at least, as much zinc as of both cadmium and copper, have been thrown down as sulphides, filtering out the precipitate and finally dissolving the zinc and cadmium in hot dilute (1:4) hydrochloric acid, and again precipitating as sulphides after diluting until the amount of free acid is not over 7 per cent. by weight.[1] Or else to nearly neutralize the acid solution with soda, and then pour it into a solution of caustic soda according to Fresenius[2] to separate the cadmium as hydroxide. In either case, the zinc filtrates are combined and prepared for titration by adding ammonium chloride and hydrochloric acid as usual.

The following method, developed in our laboratory, gives exact results in a shorter time than any that we have experimented with. As it is available for all classes of zinc ores, affording a satisfactory control upon the accuracy of the usual technical methods, it will be described in detail.

The method depends upon the separation of the zinc from manganese, iron and aluminum by means of hydrogen sulphide, under

[1] See Fresenius, Section 162, pp. 537–538, American edition.

[2] Section 162, 105, p. 542.

slight pressure, in a solution very slightly acidified by formic acid; the metals of the copper group having been previously separated by metallic iron or aluminum with simultaneous reduction of ferric salts. The operations are:

(1) *Solution.*—The calamine, willemite, franklinite, blende and other soluble minerals, or ores containing them, are decomposed by hydrochloric acid or aqua regia, with subsequent treatment and evaporation with an excess of hydrochloric or sulphuric acid to thoroughly eliminate nitrous compounds. If zinc spinels or aluminates are present, the insoluble residue must be fused with a mixture of sodium carbonate and borax glass, the fused mass dissolved and the solution added to the main one. If much silica is present, spinels are decomposed by fusion with soda in a platinum crucible, any lead sulphate present having been extracted by ammonium acetate. In the absence of silica or boric acid, the spinels cannot be decomposed by fusion with soda alone. In such case they can be decomposed by prolonged fusion with an alkaline bisulphate. Silicates, such as cinders from oxide furnaces, unchilled slags and some natural silicates undecomposable by acids, must be fluxed or sintered with sodium carbonate before treatment with hydrochloric acid. It is not necessary, in any case, to evaporate to dryness to separate silica—it can be filtered off in the gelatinous state. This can be done very rapidly, after dilution with water, when the gelatinization has reached a maximum and before dehydration has begun. The gelatinous silica at this stage will not retain any traces of metals after a few washings.

(2) *Reduction.*—To avoid the effects of reactions like

$$Fe_2Cl_6 + H_2S = FeCl_2 + 2HCl + S,$$

and at the same time to remove copper, silver and bismuth before precipitating with hydrogen sulphide, the filtered solution, made fairly acid with hydrochloric or sulphuric acid, is boiled for fifteen or twenty minutes with a strip of clean sheet iron or steel. By this treatment all of the metals likely to be precipitated with zinc as sulphides are separated, except cadmium, which is not in the least degree reduced by metallic iron.

Mr. G. C. Stone has suggested the use of metallic aluminum for the reduction. This has the advantage of separating cadmium and lead along with the other metals of the copper group, since

both are completely precipitated by aluminum from a rather strongly acid boiling solution of sulphates or chlorides, so that, when zinc only is to be determined, the subsequent operations are very much shortened.

Reduction may also be effected by means of sodium sulphite or thiosulphate, when copper, or copper and aluminum are to be determined from the same weighed portion.

The reduction is followed by filtration, the filtrate being received in a flask of about 300 cc. capacity.

(3) *Neutralization.*—Add to the filtrates a drop of methyl orange, then run in, from a pipette, a rather dilute solution of sodium hydroxide, meanwhile constantly agitating the contents of the flask with a swirling motion, until the pink color barely, but permanently, changes to a light yellowish tint and the cloudiness, due to the separation of hydroxides, fails to clear up entirely. Then add, drop by drop, enough 50 per cent. formic acid (sp. gr. 1.12) to just restore the permanent pink color, and add up to half a cubic centimeter additional. Dilute the solution to 200 or 250 cc. (or so that it will contain not more than 0.15 to 0.20 gram of metallic zinc in 100 cc.) and heat to about 80°.

(4) *Precipitation.*—A rubber stopper, through which passes the delivery tube from a source of supply of hydrogen sulphide, is loosely placed in the neck of the flask and a moderately rapid stream of gas allowed to pass through the hot liquid. When the precipitation of the zinc as sulphide is well under way, the stopper is pushed in tightly. Absorption of the gas ceases when all the zinc is precipitated; the precipitate settles quickly, and the gas pressure rises rapidly when the operation is completed. When several precipitations are to be made at the same time, the flasks are arranged in succession in the usual manner and the first is removed when the precipitation is well started in the third, and so on, changing the gas connections as required. The outlet from the last flask is not closed until the precipitation is partially completed therein. Numerous experiments have shown that zinc can be completely precipitated and separated from iron, manganese and alumina under the conditions named, by the passage of only a very little more than the amount of hydrogen sulphide theoretically required. The use of a large excess is therefore unnecessary and is also undesirable.

(5) *Treatment of the Precipitate.*—When the preceding operations have been properly performed, the precipitated zinc sulphide will be pure white, pulverulent and very easily filtered and washed. Hot water only need be used for washing, no zinc will dissolve, or pass through the filter, as is the case with the slimy zinc hydrosulphide precipitated from cold solutions in the usual manner. Pour the contents of the flask upon a filter at once and wash with hot water. Spread the filter with its contents upon a large watch-glass or on the inner wall of a capacious beaker, and wash the precipitate into the bottom of the beaker by a jet of hot water. Wash the precipitating-flask and the lower end of the gas delivery tube with 10 cc. of strong hydrochloric acid, followed by hot water, pouring the acid and washings successively over the washed filter on to the precipitate in the beaker. When the volume of the acid solution has reached 125 to 130 cc., the solution is warmed gently to dissolve the zinc sulphide completely.

When cadcium is also present (*i. e.,* when the reduction has been effected by metallic iron) the zinc sulphide will dissolve completely before any cadmium sulphide is dissolved. By practice and experience, the point when all the zinc is dissolved and only the brilliant yellow cadmium sulphide remains, can easily be distinguished. The solution is then further diluted with an equal volume of hydrogen sulphide water, allowed to settle and the cadmium sulphide filtered off and estimated in the usual way by warming with acid ferric sulphate and titrating with permanganate. The iron equivalent of the permanganate used multiplied by 1.003 equals the cadmium. Properly performed, the result is accurate.

The solution of zinc sulphide in dilute hydrochloric acid is heated to 60° or more, made up to 200 or 250 cc. with hot water, a little ammonium chloride added, and it is ready for titration with ferrocyanide.

The method of separating zinc by hydrogen sulphide from nickel, cobalt and manganese, recommended by Fresenius,[1] is not applicable when iron is present, as iron is thrown down by hydrogen sulphide in the presence of sodium acetate.

Modification (*c*). *For Low-grade Zinc Ores, Slags, Furnace Residues, etc.,* and for all purposes wherein it is required to determine small amounts of zinc with accuracy.

[1] American edition, Sec. 160, pp. 74 and 75.

Proceed exactly according to the method just described untll the zinc sulphide precipitate has been washed, then, instead of dissolving the precipitate, dry and ignite it carefully in a clean muffle without separating it from the paper. No loss of zinc will occur, nor will basic sulphate be formed, if the wet precipitate is ignited at the mouth of the muffle until the paper is consumed, and the oxidation of the residue is then conducted at a low temperature (about 450°) until at the last, when it may be moved back to where the temperature is near the melting-point of silver. As much as 0.15 gram of zinc sulphide can be completely oxidized in this way in forty to sixty minutes. The calcination may be effected in a smooth shallow scorifier an inch and a half in diameter, from which the calcined oxide can be brushed into the scale pan without appreciable loss.

Lime and magnesia can be determined in the ammoniacal solution of zinc obtained after iron and alumina have been separated, according to the first of the above methods or its modifications, provided it is made very strongly ammoniacal, then heated to boiling before the addition of ammonium oxalate to precipitate the lime. The solution of ammonium oxalate should also be boiling when added to the zinc solution. Enough of the oxalate must be added to convert the zinc and magnesia to oxalates, as well as to combine with the lime: 1 part zinc requires 1.0447 parts ammonium oxalate; 1 part magnesium oxide, 3.9794 parts ammonium oxalate; 1 part calcium oxide, 2.8607 parts ammonium oxalate.

The filtrate from the calcium oxalate is then to be cooled and treated in the usual manner with phosphate to precipitate magnesia. No zinc will be thrown down, if sufficient ammonia and ammonium chloride are present. The zinc in the filtrate cannot be determined by titration, but must be precipitated as sulphide; or as phosphate, by rendering the cold solution slightly acid with sulphuric or hydrochloric acid, adding a *large* excess of ammonium sodium hydrogen phosphate, neutralizing very carefully with ammonia drop by drop, adding a drop or two additional, then about 1 cc. of acetic acid and warming gently until the flocculent precipitate of $ZnNH_4PO_4 + H_2O$ has settled completely as a dense crystalline powder, which, after washing with hot water, may be dried at 100°-105° and weighed as $ZnNH_4PO_4$

containing 37.28 per cent. Zn,[1] but the better way is to ignite and weigh as $Zn_2P_2O_7$, containing 42.77 per cent. Zn. In this case the filter-paper should be burned first to ash, then the ash and dried precipitate ignited gently at first, then for a few minutes at a bright red heat.

The flocculent $ZnNH_4PO_4 + H_2O$ is very soluble in the mineral acids as well as in ammonia, but after crystallization it is much less soluble in the latter. It is only slightly soluble in acetic acid; an excess of 1 cc. in 100 cc. of solution does not dissolve an appreciable quantity. It is somewhat soluble in all ammonium salts, if only a small excess of phosphate is present. The addition of 1 cc. of a 10 per cent. solution of sodium ammonium phosphate for each 0.005 gram of zinc is sufficient to entirely prevent its solution in ammonium chloride or sulphate, or in the acetate, unless the latter is present in enormous quantity. It is, however, always slightly soluble in the oxalate. Therefore, for very accurate work, lime and magnesia, if present in the zinc solution, are preferably separated together as phosphates, after adding a large excess of ammonia and reprecipitating; then the combined filtrates are to be slightly acidulated and proceeded with as above. The crystalline zinc ammonium phosphate is quite insoluble in hot or cold water.

For this elegant and accurate, but too little known, method I am indebted to Mr. Geo. C. Stone, who has carefully worked out its details, including the properties of the precipitate. Hundreds of filtrates from zinc phosphate, separated as described, have been tested by him with ammonium sulphide, without showing zinc.

THE ORGANIC MATTER IN SOILS AND SUBSOILS.

By F. K. Cameron and J. F. Breazeale.

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INTRODUCTION.

The relative amount of organic matter in a soil or subsoil has long been regarded as an important characteristic. Popularly, and with some reason, it has been generally held to furnish an indication of the fertility of a soil. It has a real importance, since it affects the texture or structure and water-holding capacity of

[1] It can also be accurately titrated with ferrocyanide after solution in hydrochloric acid with addition of ammonium chloride. Also, according to P. H. Walker (This Journal, **23**, 468), its zinc content may be determined alkalimetrically.

the soil, serves, in part at least, as a carrier of plant food, and also serves as a host medium for various organisms essential to the soil's fertility.

It has long been recognized, moreover, that the exact determination of the organic matter in a soil sample is exceedingly difficult, taxing the skill and ingenuity of analysts to the utmost. Nevertheless, so important has this determination been regarded that many experiments have been made to find either a ready method for making it, or at least one which would yield a conventional result, and which might safely be regarded as an approximation of the truth.

To this end, three general methods have found favor:

I. The "loss on ignition" method.

II. The humus method.

III. The combustion method.

The first, or "loss on ignition" method, has probably been the most used. It consists essentially in burning out the organic matter in a sample previously dried or freed from hydroscopic moisture, and taking the difference in weight before and after ignition as the weight of organic matter originally present. The method is a rapid one, and easily manipulated, but is open to the serious objection that the high temperature generally required to effect a thorough combustion of the organic matter is sufficient to drive off from the sample much water, either of "crystallization," or of "constitution." In fact, a considerable number of the minerals to be found in most soils contain hydrogen as an essential constituent, and yield water, on severe ignition, which is not replaced by the subsequent treatment with the ammonium carbonate solution or moist carbon dioxide. The amount of water thus eliminated frequently exceeds the amount of organic matter actually present, as is strikingly illustrated by the figures given in Table III. Moreover, as will be brought out more fully at another point, a by no means negligible amount of carbon dioxide, other than that combined as carbonates of the alkaline earths, is frequently eliminated by severe ignition, and not replaced by the subsequent recarbonation method.

The second method is based upon the well-known views of Grandeau as to the importance of the *matiére noiré* or humus in the soil. It makes no pretense of giving the total amount of organic matter present, even excepting undecayed twigs, roots,

and other obviously irrelevant substances. To this method, it may be objected that it is not generally agreed that the humus thus estimated is the only part of the organic matter valuable in a soil. And further, the ammonia solutions generally used very thoroughly break up the flocculation of the clay particles in the soil, so that a considerable amount of this mineral material is, of necessity, withdrawn and dried with the humus. On ignition, if it is necessary to raise the temperature materially, a large error may be introduced by loss of water from the clay, which is estimated as part of the humus.[1]

The third or combustion method consists in burning the organic matter, either in a tube with a combustion furnace, or by powerful oxidizing agencies, such as chromic acid or potassium permanganate, collecting and determining the carbon dioxide liberated by some appropriate mechanism, and then computing the organic matter from the carbon dioxide found by means of a conventional factor. The most obvious objection which may be urged against these combustion methods is in the use of this factor. On the authority of Wolf, van Bemmelen and Wollny,[2] the most popular usage is to multiply the amount of carbon dioxide found by the factor 0.471. This factor seems to be based on the assumption made as a result of Wollny's well-known investigations that the percentage of carbon in the organic matter, or rather humus of the soil, varies but little from 56 per cent. Wiley, however, states that it may vary between the wide limits, 42 and 72 per cent. An investigation of this point with typical soils of the United States will be described at another place in this paper.

COMPARISON OF THE ORGANIC MATTER IN SOILS AND SUBSOILS.

For certain lines of work being carried on in this Bureau, it is desirable to have accurate determinations of the organic matter in soils and subsoils. It has been the practice here to make determinations of the loss on ignition for this purpose. While this practice has long been felt to be far from satisfactory, it has become especially so recently, when it was found that the results thus obtained must, in many cases, be very misleading, and un-

[1] In this connection, see Frear: Bull. 67, Bureau of Chemistry, U. S. Department of Agriculture, p. 40.

[2] Wiley's "Principles and Practice of Agricultural Chemical Analysis," Vol. I. A complete historical account of this subject will be found in the work cited.

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suited even for comparative purposes. In the course of the field work of 1900, there were eighty-four cases submitted to the laboratory in which the organic matter or loss on ignition was desired in both soil and corresponding subsoil. In thirty-two of these cases, the loss on ignition method showed larger figures for the subsoils than for the corresponding soils, and often very much larger figures. It was obviously certain, in some of these cases, that the figures obtained could not give a true comparison between the soil and subsoil. Inspection did not show that this peculiarity belonged to any particular class of soils, nor did their physical characteristics throw any light upon it. The problem was then referred to the laboratory, and it was determined to compare the various methods which have been suggested, not only as to the probability of organic matter predominating in the soil or subsoil, but to obtain a procedure which would lead to more satisfactory results and, at the same time, be sufficiently rapid to meet the considerable volume of such work incident to the Bureau's investigations.

SAMPLES SELECTED FOR INVESTIGATION.

For this purpose three soils and their corresponding subsoils were selected. They were taken somewhat at random, except for the one condition that the subsoils selected had yielded larger results than the corresponding soils in earlier determinations of the loss on ignition. Determinations of the total nitrogen in these samples by the well-known Kjeldahl method were made, but in no case were quantities found sufficiently large to make it necessary to guard against nitrogen in the operations to be described. The amounts of carbon dioxide liberated by dilute sulphuric acid were also determined, and, when necessary, have been allowed for in the data given in this paper. The amounts of carbon dioxide thus liberated by dilute acid in these particular soils are so small that it was not considered necessary to remove this substance before proceeding with certain of the operations to be presently described. In the case of samples containing much carbonates of the alkalies or alkaline earths, it might be found desirable to follow the suggestion of Manning[1] and treat the moistened sample with sulphurous acid before proceeding to a determination of the organic matter, although other procedures

[1] *Vide* Wiley, *Loc. cit.*, p. 321.

also suggest themselves, which, for some conditions, are probably more advisable.

Brief descriptions of the samples used in this investigation, together with the amounts of total nitrogen, and carbon dioxide liberated by dilute acid, are brought together in Table I.

TABLE I.—DESCRIPTION OF SOILS AND SUBSOILS WITH PERCENTAGES OF COMBINED CARBON DIOXIDE AND TOTAL NITROGEN.

Sample No.	Description.	Depth.	Carbon dioxide combined. Per cent.	Total nitrogen. Per cent.
4248	Conowingo clay, east of Pilot, Md..	0″– 8″	0.10	0.08
4249		8″–48″	0.17	0.12
5223	Cecil sandy loam, 2½ miles south of Raleigh, N. C.....	0″– 8″	0.00	0.08
5224		8″–36″	0.02	0.06
5861	Cecil clay, 1¼ miles north of Raleigh, N. C.....	0″– 6″	0.06	0.10
5862		6″–36″	0.06	0.04

COMPARISON OF RESULTS BY VARIOUS METHODS.

In Table II are given the results of the determinations of organic matter made in the several ways indicated.

TABLE II.—COMPARISON OF ORGANIC MATTER, HUMUS, AND LOSS ON IGNITION.

Sample No.	Loss on ignition. Per cent.	Humus, official method. Per cent.	Humus, using pump. Per cent.	Combustion, in tube, $CO_2 \times 0.471$. Per cent.	Combustion, wet way, $CO_2 \times 0.471$. Per cent.
4248	3.92	1.27	0.47	0.87	0.67
4249	6.67	1.40	0.70	0.97	0.74
5223	3.58	1.30	0.70	2.26	1.75
5224	7.63	3.45	0.30	1.47	0.68
5861	6.76	2.05	0.90	2.54	2.18
5862	11.98	2.80	0.15	0.98	0.38

The results given under "loss on ignition" were obtained by heating the test samples in a muffle furnace at a temperature of about 800° C., using platinum dishes, and recarbonating by putting the moistened soils in a chamber filled with carbon dioxide under a pressure of three atmospheres. It has frequently been found necessary to resort to such high temperatures in order to secure complete combustion of the organic matter, but an element of importance is sometimes involved, for in certain soils some iron is apparently reduced to the metallic condition, and then amalgamates with the platinum dishes. In several instances, serious damage has been done in this way, and a word of caution

is deemed worth while in this connection. When the results obtained by this method are compared with those given in the other columns, two points immediately strike the attention. First, they are all remarkably high, and if the other methods give any true index of the organic matter present, results by this method may obviously give entirely untrustworthy notions as to the composition of the samples. The second point is that in these particular cases the subsoils invariably yielded higher figures than the soils. This point will be discussed more fully at another place, but it is of importance here to point out that it does not give a true index of the *relative* amounts of organic matter in the soils and subsoils respectively, and this fact is thus another valid and important objection to the use of the method.

In the next column are given the results for humus obtained by the method of the Association of Official Agricultural Chemists. The figures, while very much lower than those in the column headed "loss on ignition," nevertheless show the same result, that the subsoils contain more organic matter or humus than the corresponding soils. But it was found in the course of these determinations that it was practically impossible to precipitate the fine sediment and clay, the flocculation of which was destroyed by the ammonia solution. Therefore, portions of the ammonia extracts were filtered through the porcelain tube of a Pasteur-Chamberland filter, by means of a simple arrangement of a Bunsen filter flask and a good water aspirator. Proper precautions were, of course, taken to have no contact of the solution with rubber connections and discard first runnings from the filter-tube, etc. It is not certain that some of the dissolved humus may not have been absorbed or otherwise removed from the solution by this procedure, but we had no evidence that such was the case, and believe that any error from this source must have been relatively small. Humus determinations on aliquot portions of the clear solutions thus obtained were carefully made, and the results are given in the table. In every case they are much smaller than when the official method was followed literally, and the conclusion seems inevitable that the higher values were occasioned by the loss of water or volatile materials other than humus, in the ignition of the clay and sediment obtained on drying the ammonia solution extracts. Another point is that in this last

column of figures we no longer find higher values for the subsoils than for the corresponding soils, except in the first pair. Since these results were believed to give a more accurate idea of the constitution of the soils than those previously described, but could not be regarded as satisfactorily giving quantitative ideas as to the whole amounts of organic matter present, and in view of the well-known wide divergence of opinion as to the value of humus determinations, it was decided to investigate the soils by the combustion method. Moreover, humus determinations are, at the best, tedious to make, especially if recourse must be had to the filter, and as it is very desirable in our work to make annually a very large number of determinations of the organic matter in soils, it was the more desirable to see what could be done with a combustion method. We first employed the regular method of burning the soil in a tube in a combustion furnace. The sample, which was generally about 2 grams in weight, was mixed with several times this weight of well-pulverized black oxide of copper, and the two thoroughly incorporated by grinding and stirring in an agate mortar. The usual precautions were observed in the burning, sweeping out the last traces of carbon dioxide from the tube, making weighings, etc. It was not deemed worth while to put in a guard for nitrogen or chlorides. The figures given in Table II are averages of duplicate determinations. Here again the Conowingo clay appears to contain more organic matter in the subsoil than in the soil, but the reverse is the case with the other soils examined. It is worthy of note also, that in the majority of cases the figures found are less than those obtained for humus by the official method, but are greater in every case than the corresponding figures for humus obtained when the filter was used.

Two objections to this method became patent in its use. It is obviously a matter of extreme difficulty and uncertainty to get a fair sample of soil of as small a weight as 2 grams. Larger quantities than this could not be advantageously handled in a combustion tube, however, and no other reliable form of apparatus suggested itself. Again, a combustion in a tube is necessarily a slow process, and much time which the operator cannot employ otherwise to advantage, is lost in the gradual heating and cooling of the tube necessary for its satisfactory use. A possible third objection, which we believe from our work has an actual exist-

ence, is the liberation of carbon dioxide other than that combined as carbonates of the alkaline earths, or formed in the combustion of the organic matter. This point will be more fully discussed presently.

THE CHROMIC ACID METHOD.

From the facts just presented, it was deemed advisable to study other methods. Two wet methods suggest themselves, oxidation with chromic acid or with potassium permanganate. Both of these methods have been tried to some extent.[1] The chromic acid method presents the lesser amount of manipulation, fewer analytical difficulties, and would seem to be more certain in its oxidation of the organic matter. Therefore, it alone was used in this investigation. The combustion was effected in a round-bottomed flask of about 400 cc. capacity, fitted with a 3-hole rubber stopper. The stopper was fitted with a dropping funnel, a tube for the introduction of air previously freed from carbon dioxide, and a tube leading through a condenser to a train of absorption bulbs. This train contained, first, a Peligot tube containing a saturated and slightly acidified solution of silver sulphate to absorb both hydrochloric acid and sulphur tri- or dioxide should they be generated; then a guard tube containing concentrated sulphuric acid, followed by a potash bulb and acid bulb to be weighed with the potash bulb. The whole apparatus was attached to an aspirator so that air free from carbon dioxide could be drawn through the combustion flask and train. The procedure is as follows:

A sample of the soil, usually about 10 grams, is carefully weighed and brought into the combustion flask. If the sample be rich in organic matter, it has been found advisable to introduce also some sand, previously ignited before the blast, and in an amount dependent roughly upon the apparent quantity of organic matter in the soil. From 5 to 10 grams of pulverized potassium bichromate are then added, and the whole mixed thoroughly by shaking, care being taken to prevent any of the mixture adhering to the sides of the flask, above the level of the mixture. The flask is closed securely by the stopper, and a gentle stream of air drawn through the whole apparatus by means of the aspirator. When this stream of air has been passing for about ten minutes, concentrated sulphuric acid (sp. gr. about 1.83) is slowly and cautiously run in by means of the dropping

[1] Wiley's "Principles and Practice of Agricultural Chemical Analysis," Vol. I, p. 316.

funnel until the tip of the glass tube, for the introduction of air, is covered. When this point has been reached, and if no very vigorous action is taking place, the combination flask is slowly heated until the sulphuric acid commences to give off fumes. It is held at this temperature for from five to ten minutes, and then allowed to cool slowly, unless there is reason to believe combustion has not been complete, in which case the temperature is again raised. Care must be exercised to see that a steady current of air be kept passing through the apparatus, and that the mixture in the flask be not forced back towards the wash-bottles. If necessary, quite a rapid stream can be drawn through the absorption bulbs without much risk of losing the determination. It is advisable to have the bulb of the dropping tube empty, before commencing the heating, so that the tube can be quickly opened. In over four hundred experiments with this method the flask broke but once, and then the dropping-funnel could not be opened because it contained a quantity of sulphuric acid. A sudden large increase of pressure was generated in the flask, owing to faulty manipulation. The dangerous character of such an accident is sufficiently obvious, but with ordinary care, liability of its occurrence is extremely small.

MODIFICATIONS FOR SOILS CONTAINING CHLORIDES AND CARBONATES.

In many soils from arid, semi-arid, or marshy areas, there is a considerable content of chlorides. By following the procedure just described with these soils, chlorine gas may be generated, which would be collected in the potash bulbs, forming a mixture of the chloride and hypochlorite in proportions difficult to accurately estimate, and vitiating any attempt to determine the amounts of carbon dioxide absorbed. We have made a number of attempts to get around this difficulty, and have found that it can be met quite simply. If the bichromate of potash be not mixed with the sample before running in the concentrated sulphuric acid, but be dissolved in the acid itself and the solution be slowly and cautiously run in upon the soil, with no attempt to heat the mixture until the reaction in the flask has proceeded for some time, no hydrochloric acid, chlorine, nor chromyl chloride gas is generated, or in but very small amounts. The procedure thus modified has been used a large number of times with

artificial mixtures and natural soils, and has proved satisfactory, although no explanation is obvious why hydrochloric acid should not be formed and oxidized under these conditions. We can only say that, although we discovered the fact empirically, we have thoroughly tested it with the most gratifying results for the method.

When the amount of chlorides is relatively large, it has sometimes been found desirable to treat the sample with a small volume of dilute sulphuric acid, adding more acid in small quantities from time to time, if necessary, to digest on the steam-bath until the major part of the hydrochloric acid has been removed, and to evaporate as much of the water remaining as can be done without permitting a noticeable action of the solution upon the organic matter. The combustion is then carried out as above described.

With soils which contain carbonates of the alkalies or alkaline earths, it would probably be found satisfactory, as indicated above, to first treat with sulphurous acid to decompose the carbonates, and drive out the carbon dioxide, without oxidizing the organic matter and then to get rid of the water and sulphurous acid by evaporating to dryness before proceeding with combustion.

This method presents, however, a number of difficult manipulations, and requires a great deal of time. It has been found, in the experience of this laboratory, much more convenient to make a separate determination of the carbon dioxide liberated from carbonates, by treating a separate sample of the soil with dilute sulphuric acid (1 : 6 by volume), and subtracting the amount thus found from the total obtained in the combustion. While this method is not entirely free from objections for very accurate work, it does unquestionably lead to values with all the accuracy necessary for most purposes to which the determination of the organic matter in a soil is applicable.

TABLE III.—WET COMBUSTION OF KNOWN ORGANIC SUBSTANCES.

Substance. Formula.	Weight taken. Gram.	Carbon dioxide found. Gram.	Weight found. Gram.	Per cent. recovered.
Sugar, $C_{12}H_{22}O_{11}$	0.5026	0.7669	0.4984	99.16
	0.4465	0.6865	0.4462	99.94
Cellulose, $C_{12}H_{20}O_{10}$	0.4300	0.6633	0.4073	94.7
	0.4232	0.6272	0.3849	90.9
	0.4135	0.6255	0.3840	92.8
	0.3714	0.5680	0.3487	93.9
	0.3430	0.5205	0.3192	93.0

Substance. Formula.	Weight taken. Gram.	Carbon dioxide found. Gram.	Weight found. Gram.	Per cent. recovered.
Urea, CH_4N_2O	0.7858	0.5590	0.7636	97.17
	0.7090	0.4990	0.6816	96.14
Asparagine, $C_4H_8N_2O_3.H_2O$ ..	0.5035	0.5945	0.5071	100.71
	0.4704	0.5600	0.4776	101.53
Sulphanilic acid, $C_6H_7NSO_3$..	0.4080	0.6220	0.4080	100.0
	0.2115	0.3201	0.2100	99.29

TEST OF THE CHROMIC ACID METHOD WITH KNOWN ORGANIC SUBSTANCES.

Objection has been urged to the method, that it does not, or at least may not, give accurate results, because some organic substances are not completely oxidized by the chromic acid mixture. With some organic compounds and with the chromic acid mixture as generally used, *i. e.*, containing one or more parts of water to every three of sulphuric acid, this is unquestionably true, even when the temperature is raised considerably. But when the procedure is followed, in which only a minimum of water is present, derived from the hydroscopic water in the soil, from the bichromate used, and the product of combustion, it is not believed such an error enters. To test this point, various organic substances of widely different characteristics were burned according to the method just described. In order to distribute the acid mixture, the substance under examination and the bichromate of potash were shaken up with from 10 to 15 grams of ignited sand, after being introduced into the flask. The results are given in Table III. While in some instances, certainly, these results cannot be considered as entirely satisfactory determinations when compared with the standard obtainable by the regular method of burning in a tube, they do show that very fair results are obtained, and that there is no reason to expect such phenominally low results as have been reported by other analysts when employing a wet combustion. Sulphanilic acid, for instance, when treated with the chromic acid mixture as commonly used, as is well known, is largely converted into quinone, but no difficulty was experienced in burning it completely, with such satisfactory results, as the figures in the table show.

The cellulose used was a sample of "double washed, ashless" filter-paper. The values obtained with this substance, as shown in the last column of the table, were so low that two combustions of it were made in the tube in the regular way, with the result

that 96.9 per cent. and 96 per cent. of the amounts taken were recovered as calculated from the weights of carbon dioxide obtained. Evidently this particular substance we had was not well chosen as a representative sample of cellulose, and the figures given in the table are actually better than they appear, though showing an undoubted tendency to run low.

The sample of urea used had been standing a long time in the laboratory. A small portion was recrystallized, and this product gave a much more satisfactory figure for the single combustion of it which was made; but it was believed to be more satisfactory to give the two results from the original sample as showing that the method would give concordant results, especially as we had other results for nitrogenous compounds which showed that the method could be relied upon for this class of substances.

COMPARISON OF COMBUSTIONS BY THE TUBE AND CHROMIC ACID METHODS.

Combustions of the soils were then made. The averages from the determinations are given in Table II for the sake of making a more ready comparison with the other data found. The results of the individual determinations, together with those made in the tube are, however, presented in Table IV.

It should be observed, however, that the results as stated are in terms of percentages of organic matter and consequently involved the use of the factor 0.471, whereby the discrepancies are made to appear less than half of those actually obtained in percentages of carbon dioxide.

TABLE IV.—COMPARISON OF WET AND DRY COMBUSTIONS OF ORGANIC MATTER IN SOILS.

Sample. No.	In tube.		Wet way.		
4248	0.79	0.94	0.66	0.69	0.65
4249	0.97	...	0.68	0.79	...
5223	2.15	2.36	1.71	1.79	...
5224	1.47	...	0.73	0.62	...
5861	2.50	2.57	2.16	2.19	...
5862	0.98	...	0.37	0.38	0.39

It will be observed that, on the whole, better agreements were obtained by the combustions in the wet way; but, as found by analysts who have worked upon this subject, the wet way leads uniformly to lower results than the combustions in the tube. Combustions in the tube in the hands of competent analysts have

come to be regarded as almost absolute, and therefore great discredit has hitherto been cast upon combustions of soils made in the wet way. This appears to be unjust to the latter method, for the high temperature attained in the combustion tube may be expected to drive out some carbon dioxide, not derived from the oxidation of the organic matter. Ever since the classical work of Bunsen, the difficulty of getting rid of absorbed carbon dioxide except at very high temperatures, has been recognized. The minute cracks and fissures in the small rock and mineral fragments which go to make up a soil are known to contain, frequently, small amounts of carbon dioxide, which are much more likely to be given off in the highly heated combustion tube than in the wet combustion. But probably more important is the carbon dioxide combined with the iron compounds, prevalent in most soils. It will be admitted at once that the existence of iron carbonates or hydrated carbonates in the soil has, so far as we are aware, never been satisfactorily demonstrated, and that the weight of mineralogical evidence is rather against it. That carbon dioxide plays a tremendous role in the solution, transportation and redeposition of iron in the soil, can be scarcely doubted by any one who has given consideration to the subject. That some carbon dioxide would be held by these compounds, either mechanically occluded or actually in chemical combination, seems altogether probable. Such amounts of carbon dioxide would be expected to be liberated readily in the combustion tube, but not at all or not so readily in the wet method. The carbonates of iron are either not readily attacked by concentrated sulphuric acid, or only on prolonged boiling, and the mechanically held carbon dioxide would naturally be expelled much less readily in this medium than in the highly heated tube. To test this point, the soils were first burnt in the wet way. They were then filtered as rapidly as possible in Gooch crucibles, fitted with mats made from asbestos fibers, which had been thoroughly ignited before the blast-lamp. They were then washed free from sulphuric acid, as rapidly as possible, by successive small portions of distilled water. Examining by a powerful magnifying glass, in no case could any traces of organic substances be found in the residues. The residues were then dried at 110°-120° C., placed in a combustion tube and burned in the usual way, proper care being taken, of course, to free the apparatus from carbon dioxide before

commencing the burning. A portion of the original sample in each case was taken for a combustion in the tube in the usual manner. The results of this work, calculated as percentage of organic matter in the soil, using the factor 0.471, are given in Table V.

TABLE V.

Sample. No.	Combustion with chromic acid.	Combustion of residue in tube.	Sum.	Combustion in tube.	Difference.
4248	0.69	0.24	0.93	0.94	+0.01
4249	0.79	0.17	0.96	0.97	+0.01
5223	1.71	0.42	2.13	2.15	+0.02
5224	0.73	0.49	1.22	1.46	+0.24
5861	2.19	0.20	2.39	2.49	+0.10
5862	0.39	0.37	0.76	0.97	+0.21

In every case, the combustion of the residue from treatment in the wet way gave a surprisingly large increase. Taking the figures obtained as a whole, the idea seems to be amply confirmed that the combustion in the tube does yield a large amount of carbon dioxide not derived from the burning of the organic matter. The amounts obtained on the recombustions are certainly astonishing when one considers the relatively small amounts of carbon dioxide obtained from these soils by digestion in dilute acid as given in Table I. That the gas, which is thus given off and collected in the potash bulbs, could be anything else than carbon dioxide, does not seem possible.

PERCENTAGE OF CARBON IN THE HUMUS OF AMERICAN SOILS.

In view of the conflicting statements which exist as to the amount of carbon contained in the humus of soils, and the wide variation in the figures given for this amount, it was deemed advisable to make some investigation on this point with special reference to American soils.

There was available for this purpose a collection of typical agricultural soils prepared by the Bureau for the purposes of comparison, illustration and instruction. The humus was obtained from these soils in the usual way, treating them with hydrochloric acid, removing all traces of chlorides by washing with water and then extracting with 3 per cent. ammonia solution. In the vast majority of cases, the ammoniacal extract which could be decanted from the residue of soil, contained so much suspended material that it was impracticable to work upon it. Therefore it

was put through a Chamberland-Pasteur filter by which means a perfectly clear solution was obtained free from clay and other suspended material. An aliquot part of this solution was then placed in a weighed platinum dish, carried to dryness on the water-bath and desiccation completed by placing the dish in the hot air oven at 105° until constant weight was obtained. The differences between the two weights thus obtained are given in the second column of Table VI. The residue was ignited carefully until all signs of the presence of organic matter had disappeared, and the dish was again weighed, by which means it was possible to obtain the ash from the humus extract which in all cases was found to be considerable. In the third column of the table are given the percentages of the humus in the soils corrected for the ash residues which were obtained. These figures, therefore, represent presumably only the organic matter of the humus.

TABLE VI.—PERCENTAGE OF HUMUS AND CARBON IN HUMUS OF TYPICAL SOILS OF THE UNITED STATES.

Sample No.	Per cent. of humus, filtrate.	Per cent. of humus.	Per cent. of carbon in humus.
6552	0.77	0.41	43.10
2806	0.34	0.19	37.20
3994	0.86	0.63	40.65
3964	0.48	0.35	44.10
4012	0.61	0.46	46.21
4000	12.18	11.08	48.10
2809	0.39	0.09	40.31
6035	2.33	2.05	49.22
6550	0.20	0.09	44.00
3966	1.66	1.30	48.61
6548	0.36	0.16	43.46
3959	0.39	0.32	33.30
86	0.58	0.37	34.91
6551	0.26	0.08	33.30
3956	0.59	0.47	50.09
3663	1.07	0.26	44.30
2808	0.54	0.28	36.22
2791	0.32	0.18	37.41
6547	0.23	0.14	39.20

Another portion of the ammoniacal filtrate was carried to dryness and the residue was then taken for the combustion analysis. Combustions of these residues were made both in the tube by the usual method and also by the wet method described in this paper, with satisfactory agreement. The percentages of carbon in the

humus obtained from these combustions and corrected for the ash, are given in the last column of the table.

It will be seen by an inspection of this table that the percentage of carbon in the humus is much lower than the figures usually accepted, averaging about 42 per cent. instead of 56 per cent., the figure accepted by Wollny, Wolf, von Bemmelen and other authorities.

This would lead to the use of a much higher factor in the calculation of organic matter in the soil than the one employed by these investigators and used in this paper, but it does not seem desirable to advocate this higher factor. While it is probably true, as the figures here presented show, that the percentage of carbon in the humus is lower than the figure set by the authorities cited, nevertheless the amount of humus present in the soil which is extracted by ammonia, after treating with hydrochloric acid is by no means (in the majority of cases) a very large part of the total organic matter present. Furthermore, this organic matter, not extracted by the ammonia, is made up largely of cellulose or cellulose-like substances in which the percentage of carbon approaches closely the figure given by van Bemmelen.

It is impossible, in the present state of our knowledge, to suggest a fair average between the factors derived from these varying data. Inasmuch as the percentages of carbon in the soil calculated by the varying factors do not differ very much from one another, or yield differences which cannot be intelligently interpreted, it seems wisest, on the whole, to retain the factor 0.471, insisting that it is a conventional factor, and that consequently the organic matter in the soil determined by its use cannot be regarded as anything more than an approximation to the truth by a purely conventional method.

THE ASH OR MINERAL CONSTITUENTS OF HUMUS.

It seems worth while here to call attention to the considerable amounts of mineral matter dissolved in the ammoniacal extract, a large part of which is probably in organic combination. This material is unquestionably in solution, for the filtrates obtained after passing from the Chamberland-Pasteur filter are absolutely clear and free from suspended solids.

It is uncertain how much of this mineral material was in combination with the dissolved organic matter, but judging from the

figures obtained, it seems quite likely that it was largely of this nature, and it is interesting in view of the accepted practice of treating the soil with hydrochloric acid for the purpose of separating the humus bodies from the mineral constituents before extracting with ammonia.

A number of these ash residues were examined qualitatively, and in the majority of cases they were found to be made up principally of iron oxides, alumina, and silica. In several cases, considerable manganese was present in the ash, but the most striking point brought out was that in the case of certain of these soils there was unquestionably lime in the ash from the filtrate, in spite of the fact that these soils had been carefully extracted with dilute hydrochloric acid before treatment with the ammonia solution.

In the case of a residue obtained from soil No. 2809, the ash from the ammoniacal filtrate was mainly lime.

CONCLUSIONS.

(1) The conclusion seems inevitable that the combustion of a soil in the wet way with the chromic acid mixture, as described in this paper, will give a more accurate idea of the organic matter in the soil than any other method we have seen described. The method, moreover, is a fairly rapid one. It is found by considerable experience that such a combustion requires on the average about forty minutes for all operations, once the apparatus has been assembled, and that one man, working as rapidly as is consistent with good work, can make six to seven such determinations in a working day of seven hours. He can hardly make more than two satisfactory determinations in the combustion tube in the same length of time, using but one outfit.

(2) As a result of a large number of determinations, which have now been made by the combustion method here described, it may be said that the organic matter in a subsoil rarely equals or exceeds that contained in the corresponding soil.

(3) The facts presented here would suggest that the humus determination is of even more uncertain value than is usually believed.

(4) There is not sufficient ground as yet for advocating the use of any other factor than the usually accepted one for the calculation of the organic matter from the carbon dioxide obtained in the combustion.

[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT, UNIVERSITY OF NORTH CAROLINA.]

CONTRIBUTIONS TO THE CHEMISTRY OF THE RARE EARTHS.[1]

A STUDY OF PRASEODYMIUM: PREPARATION OF PURE MATERIAL—PRASEODYMIUM CITRATE.[2]

BY CHAS. BASKERVILLE AND J. W. TURRENTINE.

Received November 9, 1903.

We shall adopt in reporting investigations upon the rare earths the plan of succinctly stating in an introductory paragraph the facts observed and conclusions arrived at. Those desirous of familiarizing themselves with the details may peruse what follows at leisure. Perhaps others may care to pursue a similar course. No doubt a wider dissemination of the actual results arrived at will come about and the labors of abstractors be lessened and more accurate. Expediency influenced literary style before the twentieth century.

Synopsis. This paper contains a description of a novel method for rapidly preparing pure compounds of praseodymium. It depends essentially upon saturating a concentrated water solution of citric acid with ammonium free praseodymium hydroxide, in which the contaminating lanthanum is below 10 per cent. The solution is heated, whereby a new normal citrate is immediately precipitated and readily washed free from acid. The other procedures giving negative results were precipitations by potassium iodate, fractioning by hydrofluoric acid, gaseous hydrochloric acid, formaldehyde, fusion with potassium pyrosulphate, alkaline hydroxides, digestion in concentrated alkaline solutions, fusion with sodium peroxide, and attempts to form alums.

Fairly complete synopses of the observations leading to the breaking up of Mosander's[3] didymium into several elements have been given in an historical consideration of the rarer earths.[4] To

[1] This and the following dozen or more papers were presented in abstracts in a lecture delivered before the New York Section under the title "The Rare Earth Crusade, what it Portends, Scientifically and Technically."

[2] Presented at the Pittsburg meeting of the American Chemical Society, 1902.

[3] *Ann. Chem.* (Liebig), **44**, 125.

[4] *Science* (N. S.), **17**, 772 (1902); see also Dennis and Dales: This Journal, **24**, 425 (1902).

Dr. Carl Auer without doubt belongs the main credit of renewing interest in and stimulating the most modern assaults upon these interesting bodies. The former grew out of his patient research, resulting in the announcement of neo- and praseodymium.[1] The latter was the outcome of his development and the extensive use of mantles composed of thorium and its co-geners for artificial illumination. The intimate relationship and the reciprocal dependence of pure and applied chemistry could not find a better illustration. The commercial demand for thorium compounds especially has caused extensive mining of and geologic investigations for the better known natural compounds, as cerite and monazite, and utilization of several others, previously regarded as rare curiosities of the mineral cabinet. In the extraction of the useful thorium oxide, there have accumulated tons of crude salt mixtures of the rarer elements biding a time of commercial extraction and utilization.

The Welsbach Lighting Company, of Gloucester City, N. J., through their late chemist, the lamented Dr. Waldron Shapleigh, and his long time associate and successor, Dr. H. S. Miner, has aided scientific men frequently in generously loaning preparations extracted and often purified to a high degree. This, and a number of other researches which follow in this series, have been facilitated and rendered possible in certain cases by Mr. Miner's gratuities, and we wish here to express profound thanks.

During the preparation of pure thorium compounds it was noted (by B)[2] that a concentrated solution of citric acid, saturated with thorium hydroxide, precipitated a pure thorium[3] citrate on heating. After destruction of the carbonaceous material and re-solution of the thorium oxide, no absorption bands were observable with a strong beam of light passing through 15 cm. of the concentrated sulphate or chloride. In the preparation of thorium tetrachloride to be used in redetermining the atomic mass of thorium, a slight red in several cases and a green deposit in others (sometimes together) was formed in the hard glass tube several centimeters beyond the boat in which the mixture of carbon and oxide was heated. While the absorption spectrum has proved a most valuable means of investigating certain of the

[1] *Monatsh. Chem.*, **6**, 477 (1885).

[2] This Journal, **23**, 761.

[3] By "pure thorium" is meant the "old thorium" without considering the recent researches of Schmidt, the Curies, Crookes, Rutherford, Brauner, Baskerville and others.

rarer earths, as has been and will be pointed out, it is not as extremely delicate as one might wish. Boudouard[1] has been able to separate small amounts of neodymium from quite pure yttrium preparations by repeated fractionations when the material had long since failed to show the absorption bands of the former complex. Cleve[2] has observed the same with rather pure samarium. It has been learned in this laboratory that when quite pure neodymium and praseodymium oxides are mixed with carbon and heated to a dull red in an atmosphere of chlorine they do not give rise to volatile bodies. However, we have learned that praseodymium chloride, when subjected to a temperature sufficiently high to soften combustion tubing, evolved a greenish body.[3] Matignon[4] has also observed the same in regard to neodymium, when a pink colored deposit is formed in the cooler parts of the tube. From the color of these bodies, it was immediately assumed that in spite of the prolonged and painstaking method of preparation, our pure thorium compounds[5] still retained a trace of the constituents of didymium, which hangs on in other cases. Investigations were at once begun, therefore to learn the conduct of these elements with citric acid, the only novel feature in the method of purification not previously tested.

Before giving the result of those experiments, it may be well to state that up to that time the chlorine used had been generated by the action of pure concentrated hydrochloric acid upon recrystallized and granulated potassium dichromate. Subsequently a cylinder of pure chlorine was substituted with a complete cessation of the trouble. These red and green deposits were very small, but persisted in forming as long as the chlorine was prepared by the chromate method, and finally proved to be due to chromium. This was an observation of no little interest, as the chlorine gas was thoroughly scrubbed by passing through four wash-bottles of concentrated pure sulphuric acid (98 per cent.) and two columns of beads and one tower of pumice saturated with the same desiccating agent before entering the combustion tubing. One is immediately reminded of Crookes difficulty in preventing a back flow of mercury vapor in evacuating the bulbs for his beautiful

[1] *Compt. Rend.*, **126**, 12.
[2] *Chem. News*, **51**, 145.
[3] This will be taken up in one of the subsequent papers.
[4] *Chem. News*, **84**, 97; *Compt. Rend.*, **133**, 5, and *Chem. News*, **85**, 132.
[5] *Loc. cit.*

phosphorescence spectra examinations, when he states[1] there is "no use trusting to a solid reagent to absorb a gaseous body."

Praseodymium ammonium nitrate prepared by the method of Auer[2] was converted into the hydroxide and washed by decantation until the ammonium salts were virtually removed. Twenty-five cc. of a concentrated water solution of citric acid were saturated with the praseodymium hydroxide by shaking in a glass-stoppered bottle; the undissolved hydroxide filtered away and the green solution heated. Immediately a pale green amorphous precipitate formed, settled upon the bottom of the vessel, was easily filtered and washed with hot water.

Similar experiments were carried out with neodymium and lanthanum hydroxides. The former is about one-tenth as soluble in citric acid as praseodymium hydroxide and is not precipitated on boiling, until the solution is very concentrated.

Lanthanum hydroxide is intermediate in its solubility and not precipitated at once on boiling. It requires concentration and continued heat, although both of these substances allow tough, whitish precipitates to form, when a very strong solution is permitted to stand some days at the temperature of the room. Perhaps here we may have to do with such colloidal compounds of the rare metals as mentioned by Delafontaine.[3] This point requires investigation, however.

Numerous attempts were made to apply the observations noted to separating lanthanum from the didymiums as they occur in monazite sand and other rare earth minerals, but with little success. The lanthanum apparently causes a supersaturated solution to form, which it is difficult to precipitate by heat; further, when a precipitate forms, it contains all three of the elements[4] in all the fractions obtained.

The praseodymium ammonium nitrate contained about 10 per cent. of lanthanum. One precipitation, according to the procedure mentioned, was sufficient to give a body absolutely free from lanthanum, as shown by the arc spectrograph made with a conclave Rowland's grating, 15,000 lines to the inch and 21 feet

[1] *Chem. News.* **54**, 29.

[2] *Monatsh. Chem.*, **6**, 477.

[3] *Chem. News.* **73**, 284.

[4] The term "element" is used advisedly here, although there is no doubt of neodymium and praeseodymium being "complexes," as will be shown in later papers. At present, however, most chemists look upon these bodies as simple.

diameter.[1] This was determined frequently with that part of the spectrum which shows the strong lanthanum lines.

Praseodymium Citrate.—The body was prepared on different scales, using from a few grams of praseodymium ammonium nitrate to as much as 4 kilograms, in one place. The cold citrate solution (as much as 5 liters of the solution being used in certain experiments) was placed in a tall cylindrical precipitating jar and stirred by a water motor while the hydroxide was added to complete saturation, the agitation being continued from two to four hours. The temperature was kept down by placing the jar in running water. The turbid liquid was then quickly filtered by upward suction through an unglazed porcelain pear-shaped bomb. The beautiful, clear, leek-green solution was heated in large Jena glass beakers submerged in baths of boiling water, and filtered through a hot funnel, suction being applied at times, by means of the biscuit-ware mentioned, a most useful piece of apparatus when working on the large scale in the laboratory. The precipitate was readily and quickly washed by boiling water, in which it is insoluble (the washings being kept separate), until the fitrate was no longer acid to litmus.

The precipitate, when dried, was a loose powder, amorphous, of a beautiful pale green color. On analysis the following results were obtained:

	Found.		Calculated for (Pr 140.5)			
			$Pr(C_6H_5O_7)$.			$Pr(C_6H_5O_7).H_2O$.
Oxide (black) .	48.83	48.70	as PrO_2,		52.35	49.64
			or			or
			as Pr_4O_7,		49.90	48.49
Carbon	....	....	21.05	21.18	21.85	20.72
Hydrogen	....	....	1.46	1.86	1.52	1.44

REMARKS AND PRECAUTIONS.

Ammonia prevented the formation of this normal citrate in this manner; hence the necessity for thoroughly washing the hydroxide. The citrate is soluble in ammonium citrate. So far, we have not sought to separate the double salt which is evidently formed.

As is well known, lanthanum hydroxide and in fact most of these so-called trivalent rare earth hydroxides combine with the carbon dioxide of the air, whereby a partial solution results and

[1] Dr. W. J. Humphreys, of the Rouss Physical Laboratory, University of Virginia, kindly prepared these plates, a discussion of which he will publish in due time.

an increasing turbidity of the wash-water that is decanted, is observed, depending upon the poverty of ammonia and its salts. We avoided this by rapid working, making use of the largest unglazed porcelain suction filter made.

The filtrate from the citrate precipitate was concentrated by heat, and successive precipitates formed and were separated. They were mealy precipitates, which, on drying, formed light but tough masses, each succeeding mass being tougher than the preceding and more difficult to disintegrate into a powder. The fifth appeared in the solution as flocculent agglomerations like paper pulp and, on drying, became hard and leathery. The followng precipitates presented the same appearance and were almost white in color. The change in form and the disappearance of the green color were progressive throughout each series that was carried out. The percentage of oxide in the bodies correspondingly decreased from 48.83 per cent. to 35.77. The third precipitate gave strong lanthanum lines in the arc spectrum. They were not further investigated and are hardly worthy of the time necessary in view of the following facts.

In attempting to purify praseodymium on the large scale by this method, we observed that when the percentage of lanthanum rose above twenty no success attended our efforts. By the method of Auer[1] a large proportion of the lanthanum is first crystallized out as double ammonium nitrate. It has been observed by Dennis,[2] Bettendorff[3] and others that didymium breaks up the more readily, accompanied with less frequent formation of supersaturated solutions, difficult to handle, when lanthanum is present in notable amounts. By this modified Welsbach method, praseodymium may be readily separated from neodymium, but it is a more difficult proposition to secure the latter devoid of the former. To separate pure neodymium, Boudouard[4] and Muthmann[5] advocate crystallizing the double potassium sulphate, but this does not leave either one free from lanthanum, unless the material is subjected to a prolonged series of fractional crystallization, almost exasperating in their consumption of time, as all who have worked with these rare earths know.[6] With

[1] *Loc. cit.*

[2] This Journal, **19**, 800 (1897).

[3] *Ann. Chem.* (Liebig), **256**, 163.

[4] *Compt. Rend.*, **126**, 12; *Chem. News*, **77**, 193.

[5] *Ber. d. chem. Ges.*, **31**, 1731.

[6] A paper follows, giving a new method for freeing neodymium of lanthanum.

these facts in mind, it becomes evident at once that a quick method for the separation of 5 to 10 per cent. of lanthanum is worth while, and one that separated the praseodymium absolutely pure is most desirable. In fact, one phase most engrossing rare earth work at present has to do with finding such means for the separation of pure compounds.

Our last work was with 7 kilograms of praseodymium ammonium nitrate free from neodymium, but containing more than 20 per cent. of lanthanum. The material had undergone 300 crystallizations and came from about 100 tons of monazite. A water solution was precipitated by ammonium hydroxide in large glazed earthenware vessels (100-liter capacity), provided with spiral outlets by which, on removing rubber stoppers, the supernatant liquid might be drawn from different heights. The excess of ammonium nitrate was thus removed by two washings to prevent the attack of platinum (by its decomposition) in which the entire precipitate was ignited in portions. To decrease the percentage of lanthanum present, the method of Auer[1] proved satisfactory, and is not expensive, *viz.*, the mixed oxides were added to dilute nitric acid until almost saturated, an account being kept of the weight, and then as much more oxide added. The more basic lanthanum forms the nitrate and remains in solution, taking a part of the praseodymium, as might be expected, while the major portion of the latter oxide is undissolved. Lanthanum, of course, is still present in the undissolved portion, but in much smaller percentage. The difference in the affinity, at least towards nitric acid, is not sufficient to serve as a method for bringing about a rapid separation of these bodies in the pure state. The solution was separated by filtration, washed once or twice and the respective fractions converted into hydroxides of the earths free from ammonia. Citric acid saturated with the hydroxide from the nitrate solution gave no precipitate on boiling, while that from the undissolved oxides immediately gave an excellent separation of the citrate, yielding over a kilogram of pure praseodymium oxide on ignition. The material is absolutely free from lanthanum and as pure as that used by Jones[2] in his atomic weight determination. It may be well to state that Dr. Humphreys made the spectrographs for Dr. Jones and had the plates for comparison.

[1] *Monatsh. Chem.*, **5**, 508.
[2] *Am. Chem. J.*, **20**, 5, 345 (1898).

Although chemically pure citric acid free from lead, ammonia free from silica and sulphuric acid, and nitric acid giving no residue on evaporation, and redistilled water were used, the preparation contains such impurities as would be gathered from the containers used in the process, but they are in such small amounts as not to vitiate the results reported in several of the following papers, and of such a character that they may be readily removed at the stage it is deemed necessary.

This material as a neutral nitrate, examined at various dilutions and different thicknesses, showed an absorption spectrum that is given for the normal so-called elementary praseodymium (bands 569, 482, 469 and 443) and was used in the other work reported in this series. The absorption spectrum was examined and photographed with a Steinheil grating (14,438 lines to the inch) spectroscope, as described by Dennis.[1] The instrument is essentially the same, except that it is a size larger and has a quartz slit. The source of light used at first was a 100-candle power Edison incandescent light with a helexoid filament. Latterly we have substituted a 600-candle power arc light enclosed in a projection lantern which serves to focus the rays upon the slit. The bright lines of carbon and its impurities, once noted, do not interfere with the observations of the bands. The instrument was purchased with a grant from the Bache Fund of the National Academy.

During the progress of this work, the application of other methods for accomplishing the same object were attempted. Separating by potassium iodate, hydrofluoric acid, crystallizing a concentrated chloride solution by saturating with gaseous hydrochloric acid, formaldehyde, fusion with potassium pyrosulphate, alkaline hydroxides, digestion of rare earth[2] hydroxides in concentrated alkaline solutions, fusion with sodium peroxide, and endeavoring to form alums, were tried and they either gave negative results or such as did not warrant pursuit.

Conclusion.—Pure praseodymium compounds may be prepared by heating a saturated citric acid solution from which praseodymium citrate separates when the percentage of lanthanum is below 10, in a few hours, while by the former methods weeks or even months were required.

[1] This Journal, **24**, 415.

[2] See papers on "Lanthanates," "Neodidymates," "Double Sulphates," etc., following.

[Contribution from the Chemical Department, University of North Carolina.]

CONTRIBUTIONS TO THE CHEMISTRY OF THE RARE EARTHS.

STUDY OF NEODYMIUM: PREPARATION OF PURE MATERIAL[1]—EFFORTS TO DECOMPOSE IT INTO ITS CONSTITUENTS.

By Charles Baskerville and Reston Stevenson.

Received November 9, 1903.

Synopsis.—This paper presents a new and rapid method of freeing neodymium from lanthanum, *viz.*, fractional precipitation of the chloride solution by saturation with gaseous hydrochloric acid. A number of fractionations of the purified material were made to prove the complexity of neodymium, but without success. The methods used were, fractional precipitation by gaseous hydrochloric acid (over 100); partial decomposition by fusion of the double alkaline nitrates (23); precipitation by primary ammonium oxalate (31); solution in ammonium carbonate and precipitation with acetic acid (3); fractional precipitation by such organic bases as aniline (4), benzylamine (29), piperidine (19) and phenylhydrazine (8).

Naturally investigations were to be carried along with the foregoing, looking toward the preparation of pure neodymium compounds. It was noted that the preparation of pure neodymium salts, according to Auer's method, presented numerous difficulties and required much time and many repetitions of the process. Boudouard[2] has shown that neodymium gives a double sulphate with potassium more soluble in water than that of praseodymium and presents a more rapid separation than is perhaps possible by fractional crystallization. Muthmann and Rölig,[3] working with didymium, had from yttria, extracted from monazite sand, found weeks, after making sixty crystallizations, to obtain a neodymium sulphate containing only 0.3 per cent. of praseodymium. The oxide, Nd_2O_3, obtained by them was described as "fast weiss"—(see below).

[1] Presented in abstract at the Cleveland meeting of the American Chemical Society.

[2] *Compt. Rend.*, **126**, No. 12; *Chem. News*, **77**, 193.

[3] *Ber. d. chem. Ges.*, **31**, 1718–1731 (1898).

Reference has been made to the tentative acceptance of neodymium as an element. The agreement of the figures given for the atomic weight of neodymium by Jones,[1] Brauner,[2] and von Scheele[3] point clearly to a constant material obtained from different sources. The same was also true of didymium before the classical work of Auer von Welsbach.[4] Urbain,[5] in studying didymium had from yttria extracted from monazite sand, found not only neodymium, but such other earths as erbium and Soret's X, (holmium) members of the terbic group and a little cerium. While absorption band 469 was distinctly visible, 482 and 444 were doubtful (see papers following). Demarcay[6] and Krüss and Nilson[7] had previously made analogous observations with variations of the relative intensities of these bands. Later Demarcay[8] showed that some absorption bands have been found in didymium which appear to belong neither to neodymium nor praseodymium. Further, the presence of a certain amount of samarium causes the blue bands to disappear in a vague, hardly visible nebulosity. He concluded, as a result of a number of fractionations by different methods and examinations of the absorption bands, spark spectra (including the ultra-violet region), fluorescent spectrum in calcium sulphate and by spectral colorimeter, "in spite of statements of several chemists, neodymium is a simple body and not a mixture." Yet the work by Brauner[9] on variations in the oxides gives evidence of the complexity of that element.

Our investigation was begun with the intention of testing the nature of neodymium. Many have difficulty in assigning neodymium a satisfactory location in the periodic system. Therefore, in the event we learned that neodymium was simple, it was highly desirable to determine positively its place in the natural system.

Obviously the first step was to prepare neodymium as pure as possible. The constant associates of neodymium are lanthanum and praeseodymium, which are separated by methods which, at best, are long, slow and difficult of execution. It is very de-

[1] *Am. Chem. J.*, **20**, 345.
[2] *Proc. Chem. Soc.* (1898), No. 191, p. 70.
[3] *Ztschr. anorg. Chem.*, **17**, 310.
[4] *Loc. cit.*
[5] *Bull. Soc. Chim.* [3], **20**, 9; *Chem. News*, **78**, 74.
[6] *Compt. Rend.*, **104**, 580.
[7] *Ber. d. chem. Ges.*, **20**, 2124.
[8] *Compt. Rend.*, **126**, 14; *Chem. News*, **77**, 219.
[9] *Proc. London Chem. Soc.*, March 31, 1901.

sirable, therefore, to secure a method thorough and quick for the absolute elimination of these accompanying substances.

Five hundred (500) grams of crystalline, double ammonium neodymium nitrate were used during the preliminary trials of different methods.[1]

PARTIAL DECOMPOSITION OF DOUBLE NITRATES BY FUSION.

The classic method of Berlin[2] was applied to 200 grams of the ruby-colored crystals which had lanthanum as the main impurity and some praseodymium. The numerous variations of the directions given by Berlin, offered by subsequent workers, looking toward uniform heating and decomposition, failed to improve the process. At best, such methods of fractionation require a great amount of time and patience. The material was carried through twenty-three fractionations and, while much of the lanthanum was removed, the neodymium still contained praseodymium.

Hood,[3] discussing principles of fractioning, observed: It is evident then that fractional precipitation is a method for separating two oxides differing but slightly in basic properties. It may be the work of a lifetime, even when working on a large amount of material." Having the latter and not being assured of the temporal allotment of a chemist (thirty years), we looked for more encouraging methods.

SATURATION OF NEODYMIUM CHLORIDE SOLUTION WITH HYDROCHLORIC ACID.

The neodymium ammonium nitrate containing lanthanum as chief impurity with some praseodymium was converted into the chloride by the precipitation as hydroxide with ammonia, and washing free of the precipitant. It is inadmissible to convert the double salt to the oxide by direct ignition in platinum, as the metal is attacked. To be sure, it would appear that this contamination could be readily removed by subsequent solution of the oxide in hydrochloric acid. In practice, however, the platinum is found in the solution. The explanation of this is easily had. In the first place, Brauner[4] has shown the formation of a dioxide

[1] Obtained through the generosity of Dr. H. S. Miner, chemist of the Welsbach Lighting Co.

[2] *Scand. Naturf. 8 Möde Kjöpenhavn*, p. 448 (1860).

[3] *Chem. News*, **52**, 271.

[4] *Proc. London Chem. Soc.*, March, 1901; *Chem. News*, **83**, 197.

when the nitrate is ignited. This oxide causes the evolution of chlorine on dissolving it in hydrochloric acid with the consequent solution of the platinum. In the second place, the metal is finely divided and W. L. Dudley[1] and Mallet[2] have shown that platinum in this condition and exposed to the air *is* soluble in hydrochloric acid. In later work, where large quantities were used, large earthenware tubs of 100-liter capacity with a spiral row of decantation openings on one side were used. The hydroxide was allowed to settle and supernatant liquid drawn off, and the hydroxide washed twice with water by decantation. The decantatations were filtered free of any suspended hydroxide and the filtrate discarded.

It may be well here to call the attention of those beginning work on the rare earths to the advisability of pursuing the very safe plan of saving all filtrates until they are thoroughly tested. These filtrates were not thrown away unless 10 to 20 liters had been evaporated and ignited and showed only a trace of residue. In many cases the clear water became turbid on standing exposed to the air. This was no doubt due to the absorption of carbon dioxide, which caused the precipitation of the neodymium compound or solution of the hydroxide in the wash-water and subsequent precipitation on neutralization by the excess of ammonium hydroxide in the filtrate. The hydroxide was thrown upon a filter, dried and ignited. The unglazed porcelain filter was eventually utilized in this work, as with the praseodymium, giving most satisfactory results.

The dried hydroxide was ignited in platinum over powerful Bunsen burners until no more fumes arose. The ignited product was pulverized in an agate mortar and added to the concentrated hydrochloric acid in large porcelain casseroles. The solution, which was facilitated by heat, exhibited dichroism, presenting the color of juniper swamp water (yellowish brown) with transmitted light and purple with reflected light (especially noticeable upon pouring), and faintly purple on dilution.

The neodymium chloride was filtered to remove a small gray residue of platinum obtained from the vessels and concentrated until a crust of crystals formed on top of the solution. On cooling, yellow-brown crystals appeared abundantly. They were

[1] This Journal, **15**, 272 (1893).
[2] *Am. Chem. J.*, **25**, 430 (1901).

separated, dissolved in water and the mother-liquor of neodymium chloride separately fractioned by saturation with hydrochloric acid gas.

This method of treatment possesses nothing essentially new, having been fully described previously by Dennis.[1] The gas was generated by allowing concentrated hydrochloric acid to fall dropwise upon concentrated sulphuric acid. The generator was provided with a safety-flask and the gas let into the solution by means of an inverted funnel or thistle tube which just dipped underneath the surface of the liquid.

During the early work and with the small quantities of material, only pure acids were used. When, however, later, large quantities of material (several carboys of acids) were employed, on account of the expense, commercial reagents were had recourse to. A satisfactory generator of gaseous hydrochloric acid from commercial acids was devised by one of us (Stevenson), and W. M. Marriott (of this laboratory), and is described elsewhere.

The solution was saturated with the gas until crystals appeared. The supernatant liquid was carefully decanted, the crystals washed with concentrated chemically pure hydrochloric acid, and the liquid again decanted from any crystals which subsequently formed in the mother-liquor. It was later learned that by allowing the solution to cool, the two crops of crystals could be collected in the one beaker, and washed several times with hydrochloric acid; the mother-liquor was subjected to another fractionation, crystals redissolved in the least amount of water, and fractioned again. Whenever solutions became too weak to be further fractioned, they were concentrated and subjected to the action of the gas.

During the earlier part of the work, forty-five fractionations were made and the resulting fractions classified according to the absorption spectra into four large solutions; the extreme crystals, medium crystals, medium solutions and extreme solutions, and into two small solutions—the pene-extreme crystals and the pene-extreme solutions. These solutions were fractioned as before, except that the application of the gas was continued until no more crystals appeared and the "crisscrossing" preceded each fractionation.

After twenty-two more of such fractionations, there resulted

[1] This Journal, **24**, 421 (1902), and previously.

four fractions: Extreme crystals, a very large fraction; medium crystals, about two-thirds as large; medium solutions, a moderate-sized fraction; and extreme solutions, small fraction. The extreme crystals in neutral nitrate solution showed an absorption spectrum identical with the spectrum of the extreme solution, except that in the latter the band λ 460-466 had disappeared. This band belongs to samarium. The arc spectrum of the oxide from the extreme crystals showed only vanishing traces of lanthanum.[1] The oxide of the extreme solution was brown and violet. The brown portion was largely lanthanum and neodymium with some praseodymium. The method, therefore, was promising, as almost pure neodymium was obtained in the heads.

It may be well to state the result of some of our observations here for the guidance of others in the application of this method. The method was improved as follows: The concentrated neodymium chloride solution was saturated with hydrochloric acid gas until no more crystals appeared. These crystals were then dissolved to a saturated aqueous solution and refractioned. After seven such complete precipitations, the last crystals were absolutely free from lanthanum, according to the arc spectrum. This method was used on a large scale subsequently, working with as much as 8 kilograms of neodymium ammonium nitrate, using the hydrochloric acid generator of Stevenson and Marriott. Within a week, a kilogram of neodymium oxide absolutely free from lanthanum was obtained. This serves to illustrate the value of the method.

REMARKS.

During all our investigations with the rare earths, on account of their value, the fragile containers are always placed in a second large vessel in case of accidental breakage.

The precipitation with the hydrochloric acid gas sometimes began immediately, generally in about twenty minutes. In a few cases, where the solution was dilute, only after two hours and in a few very dilute solutions, not at all. The mother-liquor decanted from crystals frequently yielded another crop on standing. Oftentimes, apparently, a supersaturated solution would be had which, when poured from one vessel to another, gave rise to spontaneous crystallization.

[1] These determinations were made by Dr. W. J. Humphreys, of the University of Virginia, with the same instrument as mentioned in the praseodymium paper.

The precipitates were always crystalline. Rapid precipitation from saturated solutions gave trellised translucent crystals which appeared white in the mother-liquor. Vitreous needles resulted from the concentrated solutions; fine irridescent crystals from dilute solutions. The spontaneous crystals, especially when formed after days of standing, were handsome pyramids from 4 to 7 millimeters in length. The crystals were always more or less colored; the extreme crystals were redder and the crystals from the extreme solutions were yellowish. Sometimes the crystals appeared in alternate layers of rose and white, very likely due to a different manner of precipitation, because no difference was observed in the absorption spectra of solutions made from the two. This is no proof, however, that different substances did not separate out more or less contaminated with each other, for, as is well known, the absorption spectrum is not a final test of a fractionation. These observations were made near the time when it would become necessary for one of the authors (S.) to leave this laboratory, so that checks could not be made by means of atomic weight determinations. This work will be taken up later.

The colors of the solutions obtained in the fractionations were striking. The characteristic dichroism of the original chloride solution has been adverted to. The extreme solutions were a bright yellow in transmitted light and bright green in reflected light. The criss-crossing was determined by the color of the solutions; and the classification by color, location in the chart of the fractionations, but mainly by the absorption spectra. All these methods agreed.

The absorption spectra at first were taken of fractions as obtained without any attempt at uniform concentration. As a result, the spectra were deceptive and not comparable. Subsequently a basis was assumed for all comparisons, 1 gram of oxide being converted into neutral chloride and diluted to 10 cc. An interesting observation was made in the examination of the fractions by means of the absorption spectrum, for band λ 460-466, the strong band belonging to samarium according to Thalèn, disappeared coincident with the loss of the yellow purple dichroism.

The bands λ 569, 482, 469 and 443, characteristic of praseodymium, persisted throughout; yet, according to the arc spectrum, the praseodymium was present in a very small amount—less than

1 per cent., as shown by Jones.[1] We were so fortunate as to have in our possession some of the material used by Dr. H. C. Jones in his careful atomic weight determination of neodymium and praseodymium. The arc spectrum of the purest preparation showed traces of gadolinium and samarium in both samples, but by a comparative examination of a solution of samarium, the absorption lines of this element were not found as impurities in our purest neodymium.

The color of the oxides obtained from the different fractions presented an interesting study. Demarçay[2] states that pure neodymium is a violet-colored oxide. A pale violet oxide was given by the extreme crystals, but a lump of it had a brown core, which easily became violet upon ignition.[3] This same oxide upon recovery after use for precipitation by organic bases (see below) was a mixture of brown cinders, rose-colored scales, mole-skin dust and black specks; yet each of these, carefully picked out and separately examined, gave the same absorption bands—the true spectrum of our purest neodymium. The oxides of the extreme solutions was a mixture of lavender and brown. It sometimes became almost white upon vigorous ignition, indicating the predominence of lanthanum. Certain blue oxides were also obtained and when sufficient shall have accumulated, will be examined.[4] Perhaps this may prove to be Chroustschoff's glaukodymium. The dark oxides go into solution in nitric acid more energetically than the lavender-colored oxides, a temporary rose-colored residue being obtained.

FURTHER EXPERIMENTS LOOKING TO PROOF OF COMPLEXITY OF NEODYMIUM.

Having secured pure neodymium containing only a trace of praseodymium, we applied a few methods looking toward a determination of the nature of that element. Below are given the methods used.

PRECIPITATION BY PRIMARY AMMONIUM OXALATE.

A neutral neodymium chloride solution prepared from the pure oxide obtained according to the method given above was used. A saturated aqueous solution of ammonium oxalate was added

[1] *Am. Chem. J.*, **20**, 345.
[2] *Compt. rend.*, **126**, 14; *Chem. News*, **77**, 219.
[3] Compare Muthmann and Rölig above.
[4] *See J. Russ Phys. Chem. Soc.*, **29**, 206.

until a permanent cloudiness was obtained. About 5 cc. of saturated primary ammonium oxalate were then added, giving local turbidity, which became a mealy precipitate upon stirring. This was essentially the method used by Dennis and Dales in their work upon the purification of yttrium.[1] After twelve hours, the precipitate settled as a rose-colored powder, leaving the supernatant liquid clear. Thirty-one such fractionations were made. The last two fractions were obtained as follows: To the boiling mother-liquor 10 cc. of the primary oxalate were added and no precipitate formed, but on cooling, crystals gradually appeared. The plan of adding praseodymium oxalate crystals to induce a separation of that constituent of didymium was tried, but the solution was exhausted. The final mother-liquor was evaporated to dryness, ignited, converted into neutral chloride solution, and examined with the spectroscope. All of the mother-liquors obtained throughout the fractioning were similarly treated, as well as the precipitates. The same absorption spectrum was obtained in every case; therefore, the process was not tried more elaborately.

SOLUTION IN AMMONIUM CARBONATE AND PRECIPITATION BY ACETIC ACID.

Pure neodymium hydroxide obtained from the chloride above by precipitation with ammonia, was washed twice by decantation. Four hundred cc. of water saturated with pure ammonium carbonate were added. No perceptible solution of the hydroxide was observed. The liquid was poured off and the hydroxide washed three times by decantation. The liquid gave no precipitate with acetic acid, but on evaporation and ignition a very small residue was obtained. Converted into a neutral chloride solution, the liquid showed only the stronger absorption bands of neodymium. It was too small in amount to be made up to the standard strength adopted. The neodymium hydroxide was treated once more with 300 cc. of saturated ammonium carbonate for several days with a similar result, consequently it was abandoned.

FRACTIONAL PRECIPITATION BY ORGANIC BASES.

G. Krüss[2] fractioned certain of the rare earths with such substituted ammonias as aniline. Smith and Jefferson[3] published

[1] This Journal, **24**, 425 (1902).
[2] *Ztschr. anorg. Chem.*, III, 108 (1893).
[3] This Journal, **24**, 540 (1902).

the effect of precipitating the rare earths with aromatic bases. We endeavored to utilize their observations in making fractional precipitations similar to the work of Schutzenberger and Boudouard, and other workers in fractioning the rare earths with ammonia. E. T. Allen[1] later used certain weak organic bases for separating thorium and zirconium from iron and beryllium.

Aniline.—To a moderately concentrated, slightly acid solution of neodymium chloride, aniline was added in excess, with stirring. No precipitate appeared at once. The solution was concentrated and more aniline added. After three days, a slight white precipitate formed, adhering to the beaker. It was filtered and the filtrate treated with aniline and boiled. More aniline was added and another meager white precipitate formed. Further attempts to get a larger precipitate even after allowing the solution to stand for three months, failed. These three precipitates showed similar absorption bands and were identical with the spectrum of the diluted mother-liquor. The process was unpromising and, therefore, discontinued.

Benzylamine.—Benzylamine upon addition to a neutral neodymium chloride solution immediately gave a rose-colored, flocculent precipitate, the liquid becoming somewhat cloudy upon stirring. The precipitate settled after twelve hours and was very difficult to filter. Only eight drops of the organic base were used to get a fractional precipitation because, as stated by Smith and Jefferson,[2] the precipitation is quantitative. After twenty-nine fractionations, the solution was exhausted. Spectroscopic examination of the precipitates, the mother-liquors and the final residue, according to the methods already cited, showed nothing noteworthy and the process was not further elaborated.

Piperidine.—Piperidine acted similarly to benzylamine, nineteen fractions being carried out. The mother-liquor soon assumed a bright yellowish green color. Some of the hydroxides were rose color and some were almost pale yellow.

Phenyl Hydrazine.—The phenyl hydrazine was added in an excess to a neutral chloride solution. Gradually, in the course of twenty-four hours, there formed a dark red precipitate which adhered to the beaker and was difficult to filter. The precipitate was dissolved in concentrated nitric acid and gave a dark red

[1] *Ibid.*, **25**, 421 (1903).
[2] *Loc. cit.*

solution due to the action of the acid upon the organic base, or a decomposition product of the base. Seven fractionations, each one requiring a week, were carried out. The precipitates showed no divergence from the original, when in the form of neutral chloride solutions they were examined with the spectroscope. After the third precipitation, the filtrate became so turbid, either from decomposition products of the phenyl hydrazine, or through hydrolysis of such double compounds as are mentioned by Delafontaine, that the process was given up.

SUMMARY.

In endeavoring to prove the complexity of neodymium by fractional precipitation, in our hands the following methods failed: Fusion of the double nitrate (according to Berlin[1]); precipitation by primary ammonium oxalate; solution in ammonium carbonate and precipitation by acetic ocid; fractional precipitation by gaseous hydrochloric acid; precipitation by the organic bases—aniline, benzylamine, piperidine, and phenyl hydrazine.

The following methods are among those which will be tried in this laboratory: The use of sodium acetate and hydrogen peroxide, electrolysis, reduction by metallic magnesium, magnesium usta, treatment with mercury oxide and nitrate, copper oxide (method applied by Schutzenberger and Boudouard to cerium), dialysis and ammonium persulphate.

UNIVERSITY OF NORTH CAROLINA,
August 1, 1903.

[CONTRIBUTED FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA.]

CONTRIBUTIONS TO THE CHEMISTRY OF THE RARE EARTHS.

A GENERATOR FOR THE CONTINUOUS PREPARATION OF GASES ON A LARGE SCALE IN THE LABORATORY.

BY RESTON STEVENSON AND W. MCKIM MARRIOTTE.

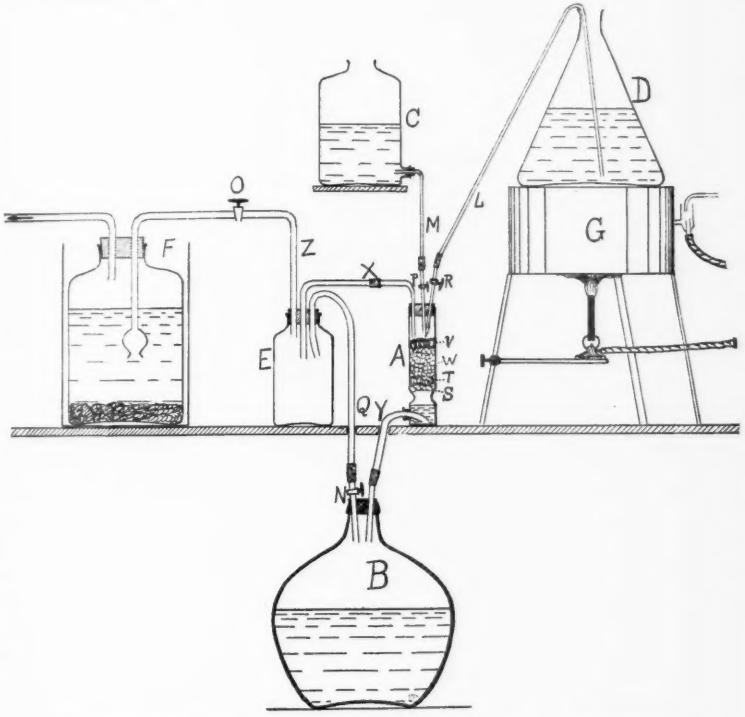
Received November 9, 1903.

A continuous stream of hydrochloric acid gas was required by one of us (S) in an investigation of the rare earths.[2] As the

[1] See preceding paper.

[2] Also modified by Dennis and Magee: This Journal, **16**, 653.

amount of gas required was large and a steady flow necessary, the apparatus here described was devised, whereby commercial acids could be utilized with consequent economy. By variation of detail, the apparatus may be used for the generation of other gases. If desirable, the gases may be dried by insertion of suitable containers for the proper desiccating agents between *E* and *F* (see figure). The whole apparatus may be readily constructed of material in any laboratory. It was used for over a month, often night and day, requiring little or no attenton, and gave perfect satisfaction.



The well-known method of generating gaseous hydrochloric acid by bringing its water solution in contact with strong sulphuric acid was found most convenient. Commercial hydrochloric acid was allowed to flow by gravity from the reservoir *C* through the

tube *M* into tower *A*. At the upper part of the constriction of *A* was placed broken cullet upon which rested glass wool. The tower was then nearly filled with glass beads, *W*, and this capped with glass wool, *V*. The tower was provided with a three-hole rubber stopper. Commercial sulphuric acid in the reservoir *D*, the bottom of which is on a level with the reservoir *C*, was siphoned through the tube *L* which projects through the stopper in *A* at an angle so that its end rests on the tube *M*, about 5 mm. from the end of the latter. These tubes are provided with stop-cocks *P* and *R* for regulating or discontinuing the flow of the acids. Allowing the sulphuric acid to flow down the tube carrying the hydrochloric acid this short distance was found to work most advantageously. The large Erlenmeyer flask *D* was placed upon a water-bath, *G*. By thus heating the commercial acid, a more rapid and larger yield of hydrochloric acid was obtained. As a mixture of acids passed through the glass wool and beads, an intimate mingling is brought about and the gas generated led through the exit tube *X* into the safety-flask *E*, from which the gas goes through *Z* into the vessel *F* in this particular case. To equalize pressure and to remove the partially spent acids, they were led from the bottom of the tower by gravity through the tube *Y* bent toward the bottom of the tower *A* into a large carboy *B*, resting on the floor. This carboy is provided with a two-holed rubber stopper through which passes the glass tube *Q* into a safety vessel *E*. By these means an equalization of pressure is had and the remaining gas generated in the waste acids obtained. Four stop-cocks, *N O P R*, were inserted for the regulation of the flow of acids or gas. The generation of the acid could be discontinued at any moment by closing them and disconnecting just beyond the stop-cock *O*. The safety-flask *E* served the dual purpose of equalizing pressure and collecting any back-flow of liquid from the precipitating vessel *F*, when such an accident occurred. Suitable rubber connections were made when necessary.

We wish to thank Professor Charles Baskerville for his interest and permisson to publish the description of the apparatus.

UNIVERSITY OF NORTH CAROLINA.

[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT, UNIVERSITY OF NORTH CAROLINA.]

CONTRIBUTIONS TO THE CHEMISTRY OF THE RARE EARTHS.

ON LANTHAN-ALUMS—SOME NEW DOUBLE SULPHATES.

BY CHARLES BASKERVILLE AND EUGENE G. MOSS.

Received November 9, 1903.

Synopsis.—This paper gives an account of some attempts, not altogether successful, to prepare lanthan-alums. The characteristic properties of lanthanum sulphate, namely, ready formation of a comparatively insoluble hydrate and double salts, appear to interfere. The following new salts, belonging to known types, were prepared: $La_2(SO_4)_3.Rb_2SO_4.2H_2O$ and $La_2(SO_4)_3.Cs_2SO_4.2H_2O$, and $La_2(SO_4)_3.Rb_2SO_4$, as well as another model, *viz.*, $3La_2(SO_4)_3.2Rb_2SO_4$ and $3La_2(SO_4)_3.2Cs_2SO_4$.

It may be recalled that lanthanum was one of the elements whose atomic weight was corrected by Mendelêeff[1] in the enunciation of the periodic law. Lanthanum is now placed in the aluminum group. Many of the sulphates of elements which form sesquioxides, form the basis of the large class of bodies known as the alums. For these two reasons it is natural to expect lanthanum to form an alum.

Locke[2] has called attention to the fact that if an element will form an alum, it does so more readily with cesium sulphate than with any of the other alkaline sulphates. Experiments were therefore begun with lanthanum sulphate and cesium sulphate in an equimolecular mixture. In endeavoring to concentrate the solution to the crystallization point by heating, either directly or by evaporation upon the water-bath, there resulted almost immediately a precipitation of the nonahydrated lanthanum sulphate, $La_2(SO_4)_3.9H_2O$. It is well-known that lanthanum sulphate deports itself in this manner. We learn also that this body fails to go back into the solution in the same amount of water on cooling. Muthmann and Rölig,[3] in their investigation on the separation of the cerite metals through the solubility of their sulphates, state that the solubility of this nonahydrate varies but slightly with the temperature.

[1] "Principles of Chemistry" (English translation), Vol. II, p. 88.

[2] *Am. Chem. J.*, **27**, 281.

[3] *Ber. d. chem. Ges.*, **31**, 1723 (1898).

As it was impossible to bring about the proper concentration of the mixture by heating, it was placed in a vacuum desiccator and allowed to evaporate under diminished pressure. Beautiful large crystals, symmetrical in form, separated out. The analysis of these crystals, from which the mother-liquor was drained, gave the following percentages:

		Calculated for		
	Found.	$La_2(SO_4)_3Cs_2SO_4.24H_2O.$	$La_2(SO_4)_3.Cs_2SO_4.$	$3La_2(SO_4)_3.2Cs_2SO_4.$
Lanthanum oxide	33.75	23.85	35.13	37.57
Cesium oxide	21.72	20.76	30.39	21.60

Another experiment was carried out by placing a similar solution in a freezing-mixture of ice and salt, but no crystals were formed.

During the progress of these experiments, efforts were made to prepare lanthan-potash alum by electrolytic oxidation. Howe and O'Neal[1] prepared iron, cobalt and chromium alums and attempted to make manganese alums by electrolysis, but without success. Later Piccini[2] prepared the cesium manganese alum by that method. This method, varied in some respects, was used with lanthanum.

A saturated solution of lanthanum sulphate was prepared by saturating sulphuric acid with lanthanum hydroxide, which had been obtained by precipitation from lanthanum ammonium nitrate. The solution of lanthanum sulphate was placed within an unglazed porcelain annealing dish. This rested in a large beaker containing more than enough double sulphate of potassium and lanthanum to make a saturated solution. It is difficultly soluble in water, hence the excess of solid. A spiral platinum cathode was placed in the solution in the annealing dish while a sheet platinum anode rested in the outer liquid. Four Lalande-Edison cells were used, giving a current of about 0.16 ampere, and the process was allowed to continue sixteen hours. No perceptible change in either the outer or inner solution was noted. A few white, opaque crystals separated about the top of the annealing cup. The solution within the annealing cup was taken out and allowed to evaporate spontaneously. In a week's time a mixture of crystals formed. The larger ones were carefully removed by tweezers and analyzed.

[1] This Journal, **20**, 764 (1898).
[2] *Ztschr. anorg. Chem.*, **20**, 12 (1899).

	Found.	Calculated for $La_2(SO_4)_3.K_2SO_4.24H_2O$.
Lanthanum oxide	27.24	27.69
Potassium oxide	8.47	8.03

This would indicate the formation of the alum. The amount obtained, 0.1868 gram, was used in the analysis. The remaining smaller crystals and some of the alums gave, on analysis, 47.37 per cent. lanthanum oxide. This indicates the coincident formation of the hexahydrate of Frerichs and Smith,[1] which carries 49.17 per cent. lanthanum oxide.

In hopes of repeating the above in another experiment with more dilute solutions the current was allowed to run for twenty-three hours. The crystals, a mixture, gave lanthanum oxide, 46.2 per cent., and potassium oxide, 9.71 per cent.

A third experiment was carried out on a larger scale, using 150 cc. of the double lanthanum potassium sulphate solution and 75 cc. of the lanthanum sulphate. The current, 0.1 ampere, was allowed to run for forty-eight hours. No crystallization took place, but four fractions were obtained in the concentration. None of them gave results on analysis worthy of mention.

Similar experiments were carried out with sodium sulphate and the current continued for fifty hours. The solutions obtained were evaporated under reduced pressure. The analysis of the crystals gave:

	Found.	Calculated for $La_2(SO_4)_3.2Na_2SO_4.18H_2O$.
Lanthanum oxide	27.40	27.41
Sodium oxide	9.78	10.47

This is doubtless a mixture and its study could not be of interest.

Another experiment with sodium sulphate was carried out with a larger current, 0.4 ampere, and continued for seventy hours. Some pretty needles separated contaminated with fine crystals. It was quite impossible to remove the former and free them from the mother-liquor—they were so soluble. The small crystals on analysis proved to be Cleve's[1] double sulphate.

	Found.	Calculated for $La_2(SO_4)_3.2Na_2SO_4+2H_2O$.
Lanthanum oxide	36.30	36.04
Sodium oxide	13.15	13.87

Experiments were carried out with rubidium sulphate. It may be remarked that it mattered not which one of the alkaline sul-

[1] *Ann. Chem.* (Liebig), **191**, 460.
[2] *Ber. d. chem. Ges.*, **11**, 912.

phates was used in the mixture; any effort to concentrate by heating always caused a precipitation of the hydrated sulphate, some double salt, or both. In a solution made of rubidium and lanthanum sulphates in theoretical amounts and evaporated in a vacuum desiccator, thin, flat silky crystals formed which, on analysis, gave:

		Calculated for	
	Found.	$La_2(SO_4)_3.Rb_2SO_4.24H_2O$.	$3La_2(SO_4)_3.2Rb_2SO_4$.
Lanthanum oxide.....	43.10	25.77	43.62
Rubidium oxide	17.64	14.78	16.77

Lanthanum sulphate is, as remarked, much more soluble in cold than in hot water, the solubility, according to Mosander,[1] being 1 part in 115 of water at 100° and 1 in 6 parts at 13°. As one of us (M.) was forced to withdraw from the laboratory, an effort was made in closing up the work to concentrate the rubidium solution at the temperature 45°-50° C. The vessel was placed in an air-bath, the temperature regulated, and the evaporation facilitated by drawing a current of dry air over the liquid by means of a suction-pump. Crystals were obtained giving a percentage of 40.4 of lanthanum oxide which would indicate the formation $La_2(SO_4)_3.Rb_2SO_4$, where the percentage of lanthanum oxide is 39.13. The body belongs to the type $Di_2(SO_4)_3,K_2SO_4$ (Marignac)[2] and $Di_2(SO_4)_3,Tl_2SO_4$ (Zschiesche).[3]

Efforts were also made to prepare an ammonium alum, but with no more satisfactory results.

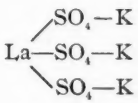
Perhaps under more suitable conditions, as spontaneous evaporation at low temperatures, the lanthan-alums may be prepared. Apparently, however, the property possessed by lanthanum sulphate of forming a stable compound with 9 molecules of water with slight elevations of temperature interferes materially with the formation of the alum. Muthmann and Rölig[4] have observed its formation at zero.

Attention has been directed by F. W. Clarke to the alum type

$$\begin{matrix} Al—SO_4—K \\ \diagdown\!\!\diagup \\ SO_4 \end{matrix}$$

and the suggestion made that lanthanum, which readily gives $La_2(SO_4)_3.3K_2SO_4$, forms the model

[1] *J. prakt. Chem.*, **30**, 380.
[2] *Ann. Chem.* (Liebig), **88**, 242.
[3] *J. prakt. Chem.*, **107**, 98.
[4] *Loc. cit.*



These specific properties of lanthanum render the formation of the alum more difficult.

UNIVERSITY OF NORTH CAROLINA.

[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT, UNIVERSITY OF NORTH CAROLINA.]

CONTRIBUTIONS TO THE CHEMISTRY OF THE RARE EARTHS.

ATTEMPTS TO PREPARE PRASEODYMIUM AND NEODYMIUM ALUMS —SOME NEW DOUBLE SULPHATES.[1]

BY CHARLES BASKERVILLE AND HAZEL HOLLAND.

Received November 9, 1903.

Synopsis.—Pure praseodymium and neodymium sulphates, *i. e.*, free from lanthanum, were prepared and attempts made to form alums by mixing with varying proportions of the alkaline sulphates. The four methods tried, *viz.*, concentration of solutions on the water-bath, in a vacuum desiccator, passing dry cold air over the solution kept at zero, and electrolysis (method of Piccini) failed to give an alum.

The following new double sulphates were prepared: $Pr_2(SO_4)_3.Cs_2SO_4.2H_2O$, $Pr_2(SO_4)_3.Cs_2SO_4.4H_2O$, and $Nd_2(SO_4)_3.Cs_2SO_4.3H_2O$, which may serve as types.

The methods of separation of lanthanum and the didymiums were not altogether satisfactory. It was thought, as these bodies are frequently classed together, that perhaps one might form an alum and serve as a method for separating them.

The alums decrease in stability with an increase in the atomic weight of the trivalent metal, while the heavier the univalent metal, the greater the stability. For instance, sodium enters into alums with the lightest of the trivalent metals, as aluminum, vanadium and chromium. On account of these characteristics and the statement made by Locke[2] that "if an alum cannot be formed with

[1] Presented in abstract at the Cleveland meeting of the American Chemical Society.

[2] *Am. Chem. J.*, **27**, 281.

cesium, it cannot be formed at all," in most of our experiments cesium was used as the univalent element.

The praseodymium sulphate was prepared from oxide obtained according to the method of Baskerville and Turrentine.[1] The neodymium sulphate was prepared from the purest neodymium oxide obtained by the method of Baskerville and Stevenson.[2]

No lanthanum was present in either of these preparations, so we hoped to avoid the difficulties encountered in the former paper. In fact, it has been stated that lanthanum might be removed in part from praseodymium and neodymium by heating the sulphates, which will bring about the separation of the lanthanum almost entirely free from the other two bodies. Muthmann and Rölig[3] made a careful comparative study of the solubility of these sulphates. While both praseodymium and neodymium sulphates are precipitated from concentrated solutions by elevation of temperature, they do not come out so readily as the lanthanum. We did not push the method to such an extent to determine if it would serve as a successful method for the separation finally, but we did learn that it would be very slow.

The praseodymium sulphate was prepared by a solution of the oxide in concentrated sulphuric acid (1:1) in platinum, the excess of acid being evaporated off by heating upon a sand-bath. The pure green crystalline praseodymium sulphate was dissolved in cold water. This standard solution contained for each cubic centimeter 0.05 gram of the sulphate. The standard solution of cesium sulphate contained 0.039 gram of sulphate per cubic centimeter. Equivalent amounts of these solutions were mixed and placed in a glass evaporating dish in a vacuum desiccator; within twelve hours pretty green crystals separated out. The liquor was poured off, the crystals dried with alcohol and ether, finally, by pressing between folds of bibulous paper.

The crystals were analyzed according to the methods usually employed in the analysis of potash alums, namely, weighed portions were dissolved in cold water, acidified with concentrated hydrochloric acid, the praseodymium hydroxide being precipitated with ammonium hydroxide; the excess was removed by boiling, filtered, washed and the filtrate evaporated to dryness. Cesium was determined as normal sulphate. A small amount of pure ammo-

[1] This Journal, **26**, 46.
[2] This Journal, **26**, 54.
[3] *Ber. d. chem. Ges.*, **31**, 1720.

nium carbonate was always added after the ammonium salts had been driven off to convert the cesium hydrogen sulphate into the normal sulphate. The praseodymium hydroxide was ignited in a platinum crucible and heated in the air with a blast-lamp to a constant weight. From a number of determinations and the amount of oxygen yielded by this greenish black residue when it was heated in hydrogen, its formula was taken as Pr_4O_7.

The first crystals obtained by the method outlined above gave, on analysis, the following:

	Per cent.
Praseodymium sulphate	61.07
Cesium sulphate	35.57
Water of crystallization by difference	3.36
	100.00

The body would, therefore, have the formula $Pr_2(SO_4)_3.Cs_2SO_4.2H_2O$. A new double salt corresponding to the type $Pr_2(SO_4)_3.K_2SO_4 2H_2O$ similar to Cleve's double lanthanum sulphate and Benedick's $Gd_2(SO_4)_3.K_2SO_4.2H_2O$;[1] but it is not an alum.

As the relationship of the two sulphates was correct, an attempt was made to increase the content of water of crystallization by mixing the sulphates at a reduced temperature; zero in the second experiment. When the mixture was kept at that temperature for sixteen hours with a rapid stream of dry air passing over it to facilitate evaporation, very soon exquisite green crystals separated out, which gave, on analysis:

Praseodymium sulphate	58.74
Cesium sulphate	37.64

or virtually the same compound.

The lowering of the temperature failing to raise the percentage of water, the third experiment was carried out at a temperature of 60° C. The beaker was maintained at this temperature by immersion in a carefully regulated water-bath. The crystals separated out very quickly and, like the others, possessed the characteristic green color. The analysis gave

Praseodymium sulphate	70.08
Cesium sulphate	26.99

While this body also contained 2 molecules of water of crystallization, the percentage of praseodymium sulphate obtained showed the presence of either a new sulphate or that the crystals analyzed

[1] *Ztschr. anorg. Chem.*, **22**, 393.

constituted a mixture of those previously described and a sulphate probably resembling the nonahydrated lanthanum sulphate.

One experiment was made looking toward the preparation of the praseodymium potassium alum. Theoretical proportions of the sulphates were mixed in a glass evaporating dish and kept in a vacuum desiccator exhausted over night. Green crystals separated out. They were dried and analyzed and the compound was found to be a double sulphate containing 4 molecules of water of crystallization.

Failing to prepare the alum by simply mixing and evaporating the sulphates at different temperatures, Piccini's[1] method of electrolysis was applied to praseodymium and cesium sulphates. A description of the method is given in the previous paper. The experiment was interrupted at the end of forty-eight hours, a few crystals having separated out at the cathode. The solution was decanted and evaporated in a vacuum desiccator. The reduced pressure was continued for several days until sufficient of the crystals were obtained for analysis.

Praseodymium sulphate	58.14
Cesium sulphate	35.67
Water of crystallization by difference	6.19

The compounds, therefore, were double sulphates with 4 molecules of water of crystallization.

The crystals that separated out at the cathode were analyzed with the following result:

Praseodymium sulphate	56.73
Cesium sulphate	33.63

This is virtually the same double sulphate.

ATTEMPT TO PREPARE NEODYMIUM ALUM.

Pure neodymium oxide obtained by the method of Baskerville and Stevenson[1] was converted into the sulphate in the same manner as described above for praseodymium. Standard solutions of this and cesium sulphate were prepared. Calculated quantities were evaporated *in vacuo*. Beautiful lavender crystals formed which were analyzed according to the same methods as given for praseodymium.

Neodymium sulphate	62.11
Cesium sulphate	32.34
Water of crystallization by difference	5.55

[1] *Ztschr. anorg. Chem.*, **20**, 12 (1899).
[2] *Loc. cit.*

The compound was therefore a double cesium neodymium sulphate containing 3 molecules of water of crystallization, $Nd_2(SO_4)_3 \cdot Cs_2SO_4 \cdot 3H_2O$.

Attempts were also made to prepare the potassium neodymium alum by electrolysis. The same method employed in preparing the praseodymium body was used. The crystals which separated out at the cathode gave, on analysis:

Neodymium sulphate	60.92
Cesium sulphate	33.08
Water of crystallization by difference	6.00

This body was also a double sulphate containing 3 molecules of water of crystallization.

Aluminum salts possess weak basicity, while the praseodymium and neodymium are, comparatively, basic.[1] This may account in part for our failure to prepare these alums. It is particularly interesting to note in considering these two so-called elements that the one gives a series of double salts with 2 and 4 molecules of water of crystallization, while the other gives one with 3.

UNIVERSITY OF NORTH CAROLINA.

[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT, UNIVERSITY OF NORTH CAROLINA.]

CONTRIBUTIONS TO THE CHEMISTRY OF THE RARE EARTHS.

LANTHANATES.

BY CHARLES BASKERVILLE AND GEORGE F. CATLETT.

Received November 9, 1903.

Synopsis.—The resemblance of lanthanum to aluminum was taken advantage of and the preparation of such bodies as the lanthanates and meta-lanthanates, hitherto not reported, described. The new substances are sodium tetra-lanthanate ($Na_2La_4O_7$) and meta-lanthanates of sodium, potassium, lithium and barium ($MH_9La_5O_{15}$). Two methods were used: Fusion of lanthanum oxide with alkaline carbonates, and prolonged digestion in a concentrated solution of the alkaline hydroxides at 100° C. These bodies do not serve as a means for the separation and purification of lanthanum.

Aluminum, which belongs to the third group in the periodic

[1] *Am. Chem. J.*, **26**, 166.

classification, may be separated from many elements by the solubility of its hydroxide in the non-volatile alkalies. This is due to the formation of soluble aluminates or meta-aluminates. It, therefore, appeared reasonable that lanthanum, which is classed with the same group, would deport itself similarly and perhaps offer a desirable new mode of separation from other or the rarer elements.

In their work on zirconates, Venable and T. Clarke[1] proposed the following methods for the preparation of this class of bodies.

I. Fusing with boron trioxide (Ebelmen).

II. Fusing with alkaline carbonates (Hjortdahl).

III. Fusing with alkaline hydroxides.

IV. Fusing with alkaline or earthy chlorides (Hjortdahl).

V. Precipitation of solutions of salts with alkaline hydroxides (Watts).

VI. Dissolving the hydroxide in strong solutions of sodium or potassium hydroxide and precipitation by dilution or by neutralization with an acid.

The process used by Ebelmen was not applicable with zirconia because that oxide does not dissolve in boron trioxide. The second and third processes given above, gave the most successful results. Water and dilute acetic acid were used to dissolve the alkali from the zirconate.

In the work on the lanthanates, those two methods, which were most successfully used by Venable and Clarke, were applied with some alterations, as will be noted in the detailed account which follows. Water was found useless as a washing medium, as, with the exception of the sodium tetra-lanthanate, the other bodies appeared to be decomposed. Acetic acid dissolved the lanthania and supposed lanthanate with equal ease, but it was used effectively in the preparation of the lithium lanthanate. Alcohol was used in most of the experiments, and, as far as could be seen, had little action on the product. In the case of the fusion of lanthania and barium hydroxide, a solution of ammonium chloride in water was used to dissolve out the remaining barium hydroxide.

The lanthanum compounds used were prepared from a quite pure lanthanum ammonium nitrate, generously loaned by H. S. Miner, of the Welsbach Lighting Company. The hydroxide was prepared from this compound by precipitation

[1] This Journal, **18**, 5; *Chem. News*, **74**, 42 and 54 (1896).

with ammonia and washing until free from that volatile alkali. As is well known, lanthanum hydroxide readily absorbs carbon dioxide from the air; hence it was kept covered with water most of the time, filtered and used fresh in each experiment. The oxide used was obtained by igniting the hydroxide obtained in platinum. Very concentrated solutions (nitrates and chlorides, neutral and acid) of varying thicknesses gave no absorption bands, showing the absence of certain of the rare earths that are likely to be present.

The analyses of the preparations were made by dissolving a definite quantity of the dried body in hydrochloric acid, precipitating the lanthanum hydroxide with ammonium hydroxide. The precipitate was thoroughly washed, burned and weighed as lanthanum oxide. The filtrate was evaporated to dryness and the alkalies or alkaline earths converted into sulphates and weighed as such. When water was determined, the material was ignited in combustion tubing and the moisture collected in a tared calcium chloride tube, dry air being drawn through. In several cases, either the washing medium failed to remove all of the carbonate used in the fusion, or some carbonate was formed when the material was exposed to the air. The carbon dioxide was determined in the ordinary alkalimeter by evolution and absorption.

EXPERIMENT I.—DI-SODIUM TETRA-LANTHANATE, $Na_2La_4O_7$.

Two grams of lanthanum oxide and eight grams of sodium carbonate were kept in a state of fusion for three hours. The reaction was carried out in a platinum crucible at the temperature of a blast lamp. At the end of the fusion, it was specked with small yellowish particles and white crystals were formed. The mass was treated with water until the wash-water was no longer alkaline, corallin being used as indicator. The white crystalline undissolved body remaining was dried at 100° and, on analysis, gave the following results:

Lanthanum oxide	88.00
Sodium oxide	8.00
Carbon dioxide	2.50
Water (by difference)	1.50
	100.00

The carbon dioxide was very probably in combination as lanthanum carbonate, $La_2(CO_3)_3$, as sodium carbonate would have

been removed by the wash-water. Accounting for the carbon dioxide as being present in this form, we have 8.64 per cent. of this carbonate or 91.46 per cent. of lanthanum and sodium oxides and water. Disregarding the water and revising the calculations, we have

Lanthanum oxide	90.99
Sodium oxide	9.00

or the ratio 2 : 1, *i. e.*, $Na_2La_4O_7$, di-sodium tetra-lanthanate, similar to the boron compound.

EXPERIMENT II.—HYDRATED MONO-SODIUM POLY-META-LANTHANATE.

Two grams of lanthanum oxide and 8 grams of sodium hydroxide were digested in a silver dish on a water-bath for thirty hours. A white mass, almost insoluble in water but decomposed by it, was obtained. Alcohol was used and the unchanged sodium hydroxide washed out; but not all of the sodium carbonate produced by the absorption of carbon dioxide from the air. The body gave, on analysis:

Lanthanum oxide	79.60
Sodium oxide	2.80
Carbon dioxide	3.00
Water (by difference)	14.6

Providing for the carbon dioxide as in the first experiment, we have $NaH_9La_5O_{15}.4H_2O$, comparable to the poly-meta-stannates in which one of the hydrogen atoms appears to have been replaced by the metal sodium.

EXPERIMENT III.—HYDRATED MONO-LITHIUM POLY-META-LANTHANATE.

Two grams of lanthanum oxide and eight grams of lithium carbonate were fused in a platinum crucible for five hours. Much difficulty was experienced in washing out the alkali, which was eventually remove by careful treatment with 5 per cent. acetic acid. The acid was subsequently removed by means of alcohol. A small amount of material insoluble in hydrochloric acid was found when it was examined. The analysis of the white body gave the following results:

Lanthanum oxide	82.9
Lithium oxide	1.2
Carbon dioxide	4.3
Water	9.8
Body insoluble in hydrochloric acid	1.3
	99.5

Allowing carbon dioxide to be combined in the form of lanthanum carbonate, as all of the lithium carbonate was washed out with the acetic acid, we have $LiH_9La_5O_{15}.2H_2O$ similar to the above, with the exception of having 2 molecules of water instead of 4.

EXPERIMENT IV.—HYDRATED MONO-POTASSIUM POLY-META-LANTHANATE.

Two grams of lanthanum oxide and 16 grams of potassium hydroxide were digested in a covered silver crucible on a water-bath for thirty hours. It was leached with alcohol, as it was found that water decomposed the material as in the case of the sodium hydroxide digestion. The white body gave, on analysis, the following results:

Lanthanum oxide	79.50
Potassium oxide	2.53
Carbon dioxide	0.40
Water	18.69
	101.12

which approximates the formula $KH_9La_{10}O_{15}.15H_2O$.

The body without doubt was decomposed during the washing; hence no value can be attached to the results obtained by analysis.

EXPERIMENT V.—CALCIUM COMPOUND.

An attempt was made to fuse calcium carbonate with lanthanum oxide, but such great difficulty was experienced in making the fusion and removing the unchanged calcium salts that the experiments were discontinued.

EXPERIMENT VI.—BARIUM POLY-META-LANTHANATE, $Ba(H_9La_5O_{15})_2$.

Barium hydroxide was substituted for the sodium hydroxide and the digestion carried out as in the first experiment. A concentrated water solution of ammonium chloride was used for leaching. The body obtained gave, on analysis,

Lanthanum oxide	75.97
Barium oxide	6.05
Carbon dioxide	2.8
Water	14.9
	99.72

or, disregarding the carbon dioxide, we have $Ba(H_9La_5O_{15})_2$.

As a result of these experiments, it appears that a number of bodies, quite complex in character, may be had, which seems to show the existence of a series of compounds of lanthanum which may be termed meta-lanthanates or poly-meta-lanthanates. At the same time it is quite evident from this and other work which immediately follows, that the methods are not suitable as a means of separation of these rare earths, and really little value can be attached to the above.

A per-lanthanate, or hydrated peroxide, $La_2O_5.xH_2O$, was obtained by fusion with sodium peroxide. Such a body has already been reported by Melikoff and Pissarjewsky.[1]

UNIVERSITY OF NORTH CAROLINA.

THE THERMAL EFFICIENCY OF A ROTARY CEMENT KILN.[2]

BY JOSEPH W. RICHARDS.

Received December 1, 1903.

THE following tests and results were obtained on a rotary cement burner, 60 feet long by 6 feet external diameter, fired by pulverized bituminous slack coal, at the plant of the Dexter Cement Company, at Nazareth, Pa.[3]

The ground cement mixture has the following composition:

	Per cent.
Silica	13.38
Aluminum oxide, Ferric oxide	6.04
Calcium oxide	41.96
Magnesium oxide	1.53
Carbon dioxide	34.65
Moisture	0.43

The burnt cement clinker contains:

	Per cent.
Silica	21.27
Aluminum oxide	6.42
Ferric oxide	3.18
Calcium oxide	66.70
Magnesium oxide	2.43

[1] *Ztschr. anorg. Chem.*, **21**, 70.

[2] Read before the Lehigh Valley Section of the American Chemical Society, in Gayley Hall, Lafayette College, Easton, Pa., November 18, 1903.

[3] The writer wishes to thank Mr. Brobst, manager, and Mr. Meade, chemist of the Company, for their coöperation, and Mr. W. S. Landis, instructor in metallurgy at Lehigh University, for his assistance in making the measurements and analysis of the gases.

The bituminous slack coal from Fairmount, W. Va., analyses:

	Per cent.
Moisture	0.60
Volatile combustible matter	38.10
Fixed carbon	53.24
Ash	8.06

The following ultimate composition of the coal was assumed from average analyses of coal from that region of similar proximate composition:

	Per cent.
Carbon	73.60
Hydrogen	5.30
Nitrogen	1.70
Sulphur	0.75
Oxygen	10.00
Moisture	0.60
Ash	8.05

The kiln turns out an average of 3635 pounds of clinkered cement per hour from 5980 pounds of mixture fed to it, producing 200 pounds of flue dust, equal to 3.35 per cent. of the weight of mixture charged.

The coal used averages 110 pounds per barrel (of 380 pounds) of cement produced, a quantity practically equal to 50 kilograms per barrel, or 2 barrels per 100 kilograms of coal. On account of the convenience of making calculations in the metric system, and of the coincidence noted above, the calculations will all be made on the basis of 100 kilograms of coal used, or per 2 barrels of cement made.

EXPERIMENTAL DATA.

Temperature of the clinker falling out of the lower end of the kiln, measured by the Le Chatelier pyrometer, 1200° C.= 2192° F.

Temperature of the waste gases in the chimney, 4 feet from the upper end of the kiln, 820° C. = 1508° F.

Sensible heat in the clinker leaving the kiln at 1200° C., measured by a calorimeter: kilogram calories per kilo 290; British thermal units per pound, 522.

Composition of the waste gases in the stack:

	Per cent.
Carbon dioxide	10.2
Oxygen	11.8
Carbon monoxide	0.2
Sulphur dioxide, Water, Nitrogen	not determined

Temperature of the atmosphere, 20° C.; saturated with moisture.

CALCULATIONS.

The object of the tests and calculations is to make a balance sheet of the heat generated within the kiln, and of its distribution, to find out the temperature of the hot gases which communicate their heat to the clinker, and the proportion of air used in excess of that theoretically needed for perfect combustion.

The items of the heat balance sheet are:

Heat Developed.

(1) Theoretical heating power of the fuel.

(2) The chemical heat of combination of the ingredients forming the clinker.

Heat Distribution.

(1) Heat in hot clinker.
(2) Heat in chimney gases as sensible heat.
(3) Heat in flue dust as sensible heat.
(4) Heat lost by imperfect combustion.
(5) Heat required to expel moisture from charge.
(6) Heat required to expel carbonic acid from carbonates.
(7) Heat lost by radiation and conduction (by difference).

Heat Developed.

(1) *Theoretical Heating Power of the Fuel.*—This was calculated from the proximate composition by the formula of F. Haas, published in Vol. II of the Report of the Geological Survey of West Virginia.[1] This calculation should be within 1 per cent. of the actual calorimetric value of the coal and gives:

Calorific power of 1 kilogram in kilogram calories, 7,900; calorific power of 1 pound in British thermal units, 14,225.

(2) *Heat of Formation of the Clinker.*—There was formed, per 100 kilos of coal burnt, 2 barrels, equals 760 pounds or 345 kilos of clinker. This contains, from its analysis,

	Kilos.
Calcium oxide	230.
Magnesium oxide	8.4
Ferric oxide	11.0

The assumption is now made that these occur as carbonates in the charge, and that the heats of combination with silica or alumina,

[1] *Mines and Minerals*, September, 1903.

to form silicates or aluminates, are 591 calories per kilo of lime and 827 calories per kilo of magnesia, as derived from the heats of combination given by Berthelot, in his "Thermochimie," Vol. II.

The heat of formation of the clinker, when heated up to the temperature at which combination takes place, is therefore

		Calories.
For the lime	$230 \times 591 =$	135,930
For the magnesia	$8.4 \times 827 =$	6,889
Total		142,819

Heat Distribution.

(1) *Heat in the Hot Clinker.*—A calorimeter containing 790 grams of water, was held under the outlet, and 95 grams of hot clinker caught in it. The weight of clinker used was determined after the experiment by filtering out the clinker, drying, heating to redness and weighing. The clinker at 1200° C. heated the water from 20.5° to 54.5°, a rise of 34°, thus giving out, in falling to 54.5°, $(790 \times 34) \div 95 = 283$ gram-calories per gram of clinker. As the prevailing outside temperature, used as a base, was 20° C., the clinker would have given out more than 283 calories had it fallen to 20°. Assuming its specific heat in this range as 0.20, the correction is $0.20 \times 35 = 7$ calories, and the total heat in the clinker above 20° C. is $283 + 7 = 290$ calories.

The total heat in the hot clinker made is therefore $290 \times 345 =$ 100,050 calories.

It may be remarked that the mean specific heat of the clinker between 20° C. and 1200° C. is $290 \div 1180 = 0.246$.

(2) *Heat in Chimney Gases as Sensible Heat.*—Analysis shows the gases to contain in 1 cubic meter, 0.102 cubic meter of carbon dioxide and 0.002 cubic meter of carbon monoxide, or, together 0.104 cubic meter of the two gases, which each contain 0.54 kilo of carbon per cubic meter. Therefore we have in gas measured cold: carbon in 1 cubic meter of chimney gas $= 0.102 \times 0.54 =$ 0.05616 kilo.

The carbon going into the gases per 100 kilos of coal burnt is as follows:

		Kilos.
Carbon in 100 kilos of coal, by analysis		73.6
Carbon expelled from the charge as CO_2:		
From calcium carbonate	$230 \times {}^{12}/_{56} = 49.3$	
From magnesium carbonate	$8.4 \times {}^{12}/_{40} = 2.5$	
		51.8
Total going into the gases		125.4

Therefore, volume of gas per 100 kilos of coal burnt, is $125.4 \div 0.05616 = 2233$ cubic meters of gas, as analyzed, calculated dry. Of this gas, 10.2 per cent. is carbon dioxide, 0.2 per cent. carbon monoxide, 11.8 per cent. free oxygen, and, by calculation, only 0.025 per cent. of sulphur dioxide, leaving 77.8 per cent. of nitrogen = 1737 cubic meters of nitrogen in the gases. Sulphur dioxide in the gas, from 100 kilos of coal $= 0.75 \times 2/2.88 = 0.5$ cubic meter. Water in gas, per 100 kilos of coal burnt:

		Cubic meters.
In charge	568 kilos $\times$ 0.0043 = 2.44 kilos =	3.0
In coal	100 kilos $\times$ 0.0060 = 0.60 kilos =	0.7
From hydrogen in coal	100 $\times$ 0.0530 $\times$ 9 = 47.70 kilos =	58.9
From water in air	17.35 $\times$ $^{100}/_{79.2}$ $\times$ $^{22}/_{138}$ =	65.4
	Total	128.0

Total gases per 100 kilos of coal burnt:

	Cubic meters.
Nitrogen	1737
Oxygen	263
Carbon monoxide	4
Carbon dioxide	228
Water vapor	128

The mean specific heat of these gases is, from the experiments of Mallard and Le Chatelier, per cubic meter (at standard conditions):

Nitrogen, oxygen, carbon monoxide	$0.303 + 0.000027\ t$
Carbon dioxide	$0.37 + 0.00027\ t$
Water	$0.34 + 0.00015\ t$

The mean specific heats of these gases, between 20° C. and 820° C., can therefore be calculated, and these, multiplied into the volumes of gases escaping, measured at standard conditions, gives the sensible heat going up the chimney, per degree of temperature of the gases:

	Cubic meters.	
Nitrogen	1737	
Oxygen	263	
Carbon monoxide	4	
	2004 $\times$ 0.325 =	651
Carbon dioxide	228 $\times$ 0.591 =	135
Water	128 $\times$ 0.463 =	59
		845 $\times$ (820 − 20) = 676,000 calories.

Of this total, a very large part is carried by the air used in ex-

cess of that needed for perfect combustion. Practically perfect combustion can be attained with a much smaller excess of air than is used above. Of the 263 cubic meters of oxygen, 2 would be needed to burn the carbon monoxide completely, leaving 261 cubic meters used in excess. This carried in with it 988 cubic meters of nitrogen and 39.5 cubic meters of moisture, and therefore carries out the following amounts of heat.

	Cubic meters.		
Nitrogen	261		
Oxygen	988		
	1249	$\times 0.325 =$	406
Water.....	$39.5 \times 0.463 =$		14
			$420 \times (820 - 20) = 336{,}000$ calories.

Leaving, as carried out by the normal gases produced, if no excess of air were used, 676,000 — 336,000 = 340,000 calories.

It is interesting to note that the ratio of air actually admitted, to air actually used, is as the nitrogen in the gases (subtracting that in the coal) to the nitrogen in the proper products of combustion, *viz.*, as 1735 to (1735 — 988), or as 2.32 to 1.

(3) *Heat in Flue Dust.*—There are 12 kilos of dust carried out per 100 kilos of fuel burnt, carrying out, therefore,

$$12 \times 0.22 \times (820° - 20°) = 2{,}112 \text{ calories.}$$

(4) *Heat Lost by Imperfect Combustion.*—There are 4 cubic meters of carbon monoxide escaping unburnt, causing a loss by imperfect combustion of

$$4 \times 3062 = 12{,}248 \text{ calories.}$$

(5) *Heat Absorbed in Evaporating the Water of the Charge.*—The charge contains 2.44 kilos of water per 100 of fuel burnt. We have already allowed for the sensible heat which this carries out, and need here allow only for the heat required to convert it into vapor, which is 593 calories per kilogram at 20° C.

$$2.44 \times 593 = 1{,}446 \text{ calories.}$$

(6) *Heat required to expel carbon dioxide from carbonates.*—

	Kilos.
Carbon dioxide from calcium carbonate.....	$= 49.3 \times {}^{44}/_{12} = 180.8$
Carbon dioxide from magnesium carbonate..	$= 2.5 \times {}^{44}/_{12} = 9.2$

To expel 1 kilo of carbon dioxide from calcium carbonate requires 990 calories, and from magnesium carbonate 407 calories, according to Berthelot's "Thermochimie."

	Calories.
$180.8 \times 990 =$	17,896
$9.2 \times 407 =$	3,732
Total,	21,628

(7) *Heat Lost by Radiation and Conduction.*—This might be experimentally determined, but only approximately. It is best found by the difference between the heat generated and the sum of all the other items of heat distribution.

RECAPITULATION.

Heat Generated.—

	Calories.
(1) Theoretical heating power of the fuel	790,000
(2) Heat of combination of the ingredients forming clinker	142,819
Total	932,819

Heat Distribution.—

	Calories.		Percentage of whole.
(1) Heat in the hot clinker	100,050	=	10.7
(2) Heat in the chimney gases:			
(*a*) In the excess air admitted 336,000		= 36.0	
(*b*) In the necessary products 340,000		= 36.1	
	676,000	=	72.1
(3) Heat in flue dust	2,112	=	0.2
(4) Loss by imperfect combustion	12,248	=	1.3
(5) Evaporation of water of charge	1,446	=	0.2
(6) Expulsion of carbon dioxide from carbonates	21,628	=	2.3
(7) Loss by radiation and conduction	119,335	=	12.8
	932,819		

REMARKS.

The interesting facts brought out by the above analysis are the following:

(*a*) The combination of the ingredients of the cinder evolves a large quantity of heat, equal to 18 per cent. of the heat developed by the combustion of the coal. This quantity is surprisingly great, but is a reality from the chemical standpoint; and, moreover, if it were left out of consideration there would be a deficit on the distribution side without making any allowance for loss by radiation and conduction. The heat of chemical combination is, therefore, an important item in the development of heat which cannot be neglected.

(*b*) The heat in the clinker represents only a trifle over one-

tenth of the heat developed in the kiln. This is a very low proportion for an industrial operation, and leaves large room for improvement and economies where fuel is dear.

(*c*) The great amount of heat carried out by the products of combustion and excess of air, amounting to nearly three-quarters of the total heat developed in the kiln, and over 85 per cent. of the calorific power of the fuel. This points to the greatest heat losses in the kiln, for if the temperature of the gases were reduced one-half by the use of a kiln approximately twice as long, the heat saved would amount to some 40 per cent. of the calorific power of the fuel. If the amount of air admitted were reduced to 10 per cent. excess instead of 132 per cent. excess as it now stands, the heat carried out by the hot gases would be reduced in that case also by an amount equal to 40 per cent. of the calorific power of the fuel. If both economies were practiced at once, the saving might amount to over 60 per cent. of the amount of fuel used.

(*d*) The loss by radiation and conduction is small, but might be considerably reduced at the lower end of the kiln by an asbestos lagging. This might not be practicable, however, if it resulted in the iron shell becoming too hot and being burnt out.

(*e*) The amount of air admitted to the kiln is found by calculation to be 132 per cent. in excess of that theoretically required for the perfect combustion of the fuel.

TEMPERATURE OF THE FLAME.

It is interesting to calculate what the maximum temperature of the mixed gases of combustion and excess of air can be in the kiln. The available heat of combustion of the fuel is 790,000 calories, and this is taken up by the products of combustion and the excess of air, *viz*:

	Cubic meters.	
Nitrogen	1737	2004 cubic meters.
Oxygen	263	
Carbon monoxide	4	
Carbon dioxide	136	
Water vapor	128	

The maximum temperature of the gases in the kiln is the temperature to which the 790,000 calories will heat these volumes of gas. Using the formulas for the specific heats of these gases, as previously used in this paper, the expression for the temperature becomes

$$t-20^\circ=\frac{790{,}000}{\left\{2004\times[0.303+0.000027(t+20)]\right\}+\left\{136\times[0.37+0.00027(t+20)]\right\}+\left\{128\times[0.34+0.00015(t+20)]\right\}}$$

from which $t = 1000^\circ$.

An extremely interesting fact is here brought out; *viz.*, that the clinker, leaving the kiln at 1200°, is hotter than the mixture of gases in the kiln. It is its heat of combination which causes this, and which accounts for the anomaly. In fact, the heat of combination probably heats the clinker even hotter than 1200°, in the interior of the kiln. In other words, when the ingredients of the cement are brought to their combination point by the gases in the kiln, a point practically about 1000° C., they ignite and combine, like a pile of anthracite coal igniting when heated to redness, and become, by their own heat of chemical combination, much hotter than the temperature to which the gases have heated them.

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DETERMINATIONS OF ALKALIES IN THE PRESENCE OF BORATES.

BY K. JACOBI.

Received September 15, 1903.

DISSOLVE 2 grams of the substance to be determined in hydrochloric acid, evaporate to dryness and bake for an hour. After cooling, add dilute hydrochloric acid, boil and filter off the silica. Precipitate iron oxide and alumina by slight excess of ammonia and the calcium oxide by ammonium oxalate. Precipitate the magnesia by ammonium phosphate and remove the excess of phosphoric acid by adding pure ferric chloride to the solution and precipitating the ferric phosphate with ammonia, which, of course, will also remove the excess of iron. Generally—at least as regards deposits in this country—when borates occur in large amounts, there are no bases other than those mentioned. Should any sulphates be present, the sulphuric acid ought to be determined separately and taken into account when the final calculation is made. Now evaporate the solution to dryness with 40-50 cc. of strong nitric acid and repeat a second time with 20 cc. to insure complete removal of ammonium salts. Take up in hydrochloric acid (strong), evaporate to dryness and repeat. After the second evaporation, add water, boil, filter into a tared platinum dish and

run slowly down to dryness. Place dish over a Bunsen burner and heat *very* gradually—it is best to have the dish covered—until finally it comes to a dull red heat, where it should be kept for ten minutes. This will render the boric acid anhydrous and expel the last traces of ammonium compounds, should any be left. Cool in a desiccator and weigh.

The contents are: Anhydrous boric acid (B_2O_3), sodium (potassium) chloride and sodium borate ($Na_2B_2O_4$). The existence of the latter is explained by the following reaction, which takes place only at high temperatures:

$$2H_3BO_3 + 2NaCl = Na_2B_2O_4 + 2HCl + 2H_2O.$$

Next dissolve the contents of the dish in hot water, cool and determine the sodium existing in the borate by titrating with N/2 sulphuric acid, using methyl orange as indicator. The total boric acid is now determined by titration with N/2 potassium hydroxide in the presence of an excess of glycerine and with phenolphthaleïn as an indicator. The sum of the boric acid and sodium oxide (in the borate) subtracted from the total weight of contents in the dish, gives the sodium chloride, from which sodium oxide is calculated (by multiplying by 0.53077) and added to the sodium oxide first determined by titration. If there is any potassium present, it must be determined in a separate portion.

EXPERIMENTAL.

Three samples of sodium carbonate of known composition were mixed with chemically pure boric acid, and hydrochloric acid was added.

	I. Gram.	II. Gram.	III. Gram.
Weight of sodium oxide in carbonate ..	0.0588	0.1176	0.2352
Weight of boric acid (approximate)....	0.1250	0.2500	0.5000

These mixtures were evaporated to dryness in a platinum dish, heated gently at first, increasing very slowly until a low red heat was reached, where they were kept for ten minutes, after which they were cooled and weighed.

	I. Gram.	II. Gram.	III. Gram.
Total weight of contents	0.1367	0.2941	0.6595

Boiling water was next added, the dish cooled and the sodium oxide titrated with N/2 sulphuric acid with methyl orange as indicator.

	I.	II.	III.
	cc.	cc.	cc.
Titrations were	0.70	1.30	1.10
	Gram.	Gram.	Gram.
which, multiplied by factor 0.0155, gives sodium oxide	0.01085	0.02015	0.01705

Phenolphthaleïn was now added with excess of glycerine, and the solution titrated with N/2 potassium hydroxide.

	I.	II.	III.
	cc.	cc.	cc.
Titrations were	2.55	5.60	13.80
Correction for glycerine	0.40	0.40	0.40
Leaving	2.15	5.20	13.40
	Gram.	Gram.	Gram.
Which, multiplied by factor 0.0175, gives boric acid (B_2O_3)	0.03763	0.09100	0.23450

The boric acid and sodium oxide were then added together in each instance and their sum deducted from the weight of the contents in the platinum dish after dehydration.

	I. Gram.	II. Gram.	III. Gram.
Weight of contents in dish	0.13670	0.29410	0.65950
Sum of boric acid and sodium oxide	0.04848	0.11115	0.25155
Leaves sodium chloride	0.08822	0.18295	0.40795
Multiplying by 0.53077 to convert into sodium oxide gives	0.04682	0.09710	0.21652
Sodium oxide found by titration	0.01085	0.02015	0.01705
Total sodium oxide found	0.0577	0.1173	0.2336
Sodium oxide taken	0.0588	0.1176	0.2336
Difference	—0.0011	—0.0003	—0.0016

Below are given three analyses of different materials. It will be seen that the figures for sodium oxide, found by actual analysis, correspond well with those found by difference.

	I.	II.	III.
Carbonaceous matter	....	....	0.63
Silica	14.88	0.19	9.71
Alumina and iron oxide	5.38	0.26	1.86
Lime	1.11	26.96	44.56
Magnesia	0.10	trace	3.65
Carbonic acid	5.12	....	33.04
Sulphuric anhydride	1.19	0.28	0.20
Boric anhydride	24.09	49.87	2.00
Moisture	14.81	0.33	....
Combined water	7.52	21.91	2.36
Sodium chloride	5.21	trace	trace
Sodium oxide	20.78	0.44	1.76

If the per cent. of the sodium oxide were taken by difference, it would be:

	I. Per cent.	II. Per cent.	III. Per cent.
	20.59	0.20	1.99
Difference	+0.19	+0.24	—0.23

Another method is to drive off the boric acid by repeated evaporations with methyl alcohol and then to determine the alkalies by one of the ordinary methods, but it is open to the following objections:

(1) The evaporation must be repeated six or seven times and even then there is some boric acid left.

(2) It leaves an undesirable residue of carbonaceous matter which is very hard to get rid of.

On this account I think the method first mentioned is to be preferred.

RAPID DETERMINATION OF BORIC ACID IN BORAX.

By K. Jacobi.

Received September 15, 1900.

The well-known method of titrating boric acid in the presence of glycerine depends upon the fact that solutions containing boric acid are neutral to methyl orange, but acid toward phenolphthaleïn and very distinctly so in the presence of glycerine. When titrated with alkali, after adding glycerine, the neutral point corresponds to the conversion of the boric acid to a metaborate, $K_2B_2O_4$. I have found that if glycerine is added to a solution of borax, the solution becomes acid toward phenolphthaleïn, and on titration, the neutral point corresponds to the formation of the metaborate, as before. It is evident that, in this case, just one-half as much alkali will be required as would have been required if all of the boric acid were in a free state. In practical effect, the reaction for titration is:

$$Na_2B_4O_7+2NaOH = 2Na_2B_2O_4+H_2O.$$

The method is as follows: Dissolve 2 to 4 grams of borax in water, add excess of glycerine, a few drops of phenolphthaleïn and titrate with N/2 potassium hydroxide. Deduct the correction for the glycerine from the number of cubic centimeters used and multiply by 0.0175. The product is one-half of the total boric acid present. Carbonates interfere with the end-reaction.

EXPERIMENTAL.

The borax used was dried for some time so as to expel part of the water and make it rich in boric acid, after which it was thoroughly mixed. Three samples of 2 grams each were first taken and worked according to R. T. Thomson's method for the determination of borax as it is given in Sutton's "Volumetric Analysis."

	I.	II.	III.
	cc.	cc.	cc.
Titration with N/2 potassium hydroxide	49.90	49.90	49.85
Correction for glycerine	0.40	0.40	0.40
Leaves	49.50	49.50	49.45
	Grams.	Grams.	Grams.
Multiplied by 0.0175 gives boric acid in 2 grams	0.86625	0.86625	0.86538
	Per cent.	Per cent.	Per cent.
Or per cent. boric acid	43.31	43.31	43.27

Average per cent. = 43.30.

Next, three samples of 4 grams each (so as to make the titration about the same) were weighed out, dissolved in water, phenolphthaleïn and glycerine added. Of the last named, as much was used as in the three first samples, thus making the correction the same. The results were:

	I.	II.	III.
	cc.	cc.	cc.
Titration with N/2 potassium hydroxide	49.65	49.60	49.70
Correction for glycerine	0.40	0.40	0.40
Leaves	49.25	49.20	49.30
	Gram.	Gram.	Gram.
Multiplied by 0.0175 gives boric acid in 2 grams (= one-half boric acid in 4 grams)	0.861875	0.86100	0.86275
	Per cent.	Per cent.	Per cent.
Or per cent. boric acid	43.09	43.05	43.14

Average per cent. = 43.09.

Making a difference of —0.21 per cent.

As can be seen from the above, all the results from the short method fall a little below the others, but this can be accounted for by the small amount of monoborate that is in most cases present in borax.

THE ELECTRICAL CONDUCTIVITY OF URINE IN RELATION TO ITS CHEMICAL COMPOSITION.

[SECOND PAPER.]

By J. H. Long.

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THE CONDUCTIVITY OF MIXED SOLUTIONS.

In an earlier paper[1] I gave some illustrations of the variations in the conductivity of the urine through a period of several days, the urine being collected and examined at definite short intervals. As this conductivity depends mainly on the sum of the inorganic constituents present and as sodium chloride is the most abundant of these, the determination in itself has but a limited importance. In some cases the value of the conductivity would be merely a rough measure of the salt consumed with the food, and the salt consumption is extremely variable.

Nearly all the other substances found in the urine have a significance very different from that of the salt. The latter is consumed and excreted as such, while the other important urinary constituents are products of metabolism, that is, of the breaking down of the digested and absorbed food materials. The organic products of metabolism are practically non-electrolytes or bodies with a very low conducting power; indeed the conductivity of a weak salt solution is materially lowered by the addition of urea and the effect of the purin bodies is practically in the same direction. Aside from the chlorides, the inorganic salts of the urine are mainly phosphates and sulphates of the alkali or alkali-earth metals and these are made up largely from the oxidation of sulphur and phosphorus of protein foods. We consume a certain amount of complex phosphoric and sulphuric acids in organic combination, in the lecithins and chondroitins for example, and small amounts of mineral sulphates and phosphates are also found in some of our foods, but these amounts are not large enough to vitiate the truth of the general proposition that the sulphuric and phosphoric acids as detected in the urine are results of certain kinds of metabolism. Now the conductivity measures the combined effect of these products of oxidation and, if it could be determined apart from the effect of the chlorides, a factor of considerable practical importance would be secured. In my

[1] This Journal, **24**, 996 (1902).

previous paper I indicated how that may be done approximately and below I wish to present further data bearing on the matter.

Approximately, the conductivity due to metabolic products may be found by subtracting from the observed conductivity that due to sodium chloride in the same solution. The chlorine may be accurately determined and calculated as chloride; then from tables the conductivity for a solution of this concentration may be found and used as a correction to be taken from the total observed conductivity, leaving the desired residual or metabolic conductivity. In this plan, however, an error is involved, because the conductivity of the chloride taken from the tables directly is that found in pure aqueous solution in absence of other salts, and is larger than the true conductivity of the chloride as it exists in the urine. It is necessary, therefore, to use as a correction the value of the salt conductivity, not in aqueous solution, but in a solution of a concentration corresponding to that of urine.

Several attempts have been made to measure the conductivity of mixtures of electrolytes and formulate the results. Most of the experiments have been made with dilute solutions and can not be used well in cases like the present one. The literature of the more important older determinations is given by Kohlrausch and Holborn,[1] while the more important recent discussions of the subject are those of Barmwater[2] and Wolf.[3] While the experimental data of these papers is not available for use in what follows, some of the suggestions of a theoretical nature were found of interest.

The non-electrolytes have some effect also, especially urea. The effect of urea on the conductivity of sodium chloride has been considered in a paper by Hantzsch,[4] but the solutions used were much less concentrated than is urine, and the results, besides, somewhat irregular. I have therefore made some new experiments in this direction which will be detailed first.

CONDUCTIVITY OF SODIUM CHLORIDE WITH UREA.

The conductivity of a pure urea solution is very low. Most of the data given are for very dilute solutions. For $v = 32$ Trübs-

[1] "Leitvermögen der Elektrolyte," p. 109.
[2] Barmwater: *Zischr. phys. Chem.*, **28**, 424.
[3] Wolf: *Ibid.*, **40**, 222.
[4] Hantzsch: *Zischr. anorg. Chem.*, **25**, 332.

bach[1] gives $\Delta = 0.08$, which is probably high. From a much stronger solution, 5 grams to 100 cc., or $v = 1.2$, I find $\kappa = 0.000012$ or $\Delta = 0.0144$. The urea used for this purpose was a product of great purity and the determination was made with fresh distilled water carefully prepared and stored to avoid outside contamination. This value is probably only a maximum. The work of Trübsbach shows a remarkable dissociation change or increase in the conductivity in his dilutions. Between $v = 32$ and 256 liters the Δ change is from 0.08 to 0.28. It will be seen below that such small values may be neglected in comparison with the conductivity of the other important urinary constituents.

Now as to the influence of the urea on these conductivities. In the paper by Hantzsch, referred to above, the molecular conductivity given for mixtures of sodium chloride with increasing amounts of urea are so irregular as to lead to the conclusion that the urea employed could not have been pure but must have contained some inorganic salts, as is usually the case. The first effect is, apparently, an increase in conductivity with addition of urea, followed by a decrease, which, however, is not marked. I have made several determinations with solutions of different urea strengths, with the following results. A standard salt solution was made containing 18 grams in 500 cc. This solution was made and used with precautions to secure the greatest accuracy. All the tests given below are based on this or similar solutions. 50 cc. of this solution diluted to 100 cc. gave, at 20°, as a mean of many close tests,

$$\kappa = 0.027315$$

Two dilutions were made with 50 cc. of the standard solution, 2.5 grams of urea being added in each case, and the volume diluted to 100 cc. At 20° I found

(1).....	$\kappa = 0.02683$
(2).....	$\kappa = 0.02684$
Mean	$= 0.026835$

The decrease in κ is here 0.000480. With a solution containing the same amount of salt and 1 gram of urea in 100 cc., I found

(1).....	$\kappa = 0.027126$
(2).....	$\kappa = 0.027128$
Mean	$= 0.027127$

[1] Trübsbach: *Ztschr. phys. Chem.*, **16**, 708.

The loss for the gram of urea is here 0.000188. The influence of the urea is therefore marked, the decrease in conductivity for the stronger urea solution being 1.76 per cent. and for the weaker 0.68 per cent. For 1 gram of urea and 2.5 grams of sodium chloride in 100 cc. the decrease in conductivity is about 0.00019, the results for the two solutions agreeing closely.

CONDUCTIVITY OF SODIUM CHLORIDE WITH OTHER SALTS.

To find the effect of other salts on the conductivity of the sodium chloride, I have taken as illustrations ammonium sulphate and sodium phosphate. A sulphate solution containing 9 grams in 500 cc. was prepared and the conductivity of this first determined in a cell having a capacity C = 8.368. The conductivities were found in a number of dilutions of this ammonium sulphate, a cell having a capacity C = 2.835 being used for the weaker solutions, the final volume of the dilution being always 100 cc. by addition of pure water. Then in a second series of tests a constant volume of sodium chloride solution was used, from the solution with 18 grams to 500 cc., along with the ammonium sulphate, the salt amounting in each case to 1.8 grams in the final volume of 100 cc. The table below gives the composition of the mixtures and the conductivities found. Some further determinations were made with stronger sulphate solutions, the results being necessary for the calculation finally required. The Kohlrausch method was followed. A large bridge with wire corrections known, was used throughout and a standard temperature of 20° maintained.

TABLE I.—SODIUM CHLORIDE AND AMMONIUM SULPHATE.

NaCl solution = 18 grams to 500 cc.

$(NH_4)_2SO_4$ solution = 9 grams to 500 cc.

$(NH_4)_2SO_4$ solution. cc.	NaCl solution. cc.	Water cc.	κ_{20} observed.	Δ_{20}.	Sum of conductivities.
5	..	95	0.001604	117.6	.....
10	..	90	0.003023	111.0	.....
20	..	80	0.005694	104.6	.....
30	..	70	0.008100	99.1	.....
40	..	60	0.010056	96.9	.....
50	..	50	0.01275	93.6	.....
5	50	45	0.02839	...	0.02892
10	50	40	0.02935	...	0.03033
20	50	30	0.03151	...	0.03300
30	50	20	0.03350	...	0.03541
40	50	10	0.03560	...	0.03787
50	50	0	0.03742	...	0.04006
..	50	50	0.027315	..	.....

With stronger ammonium sulphate solutions I have found the following data:

TABLE Ia.—AMMONIUM SULPHATE.

$(NH_4)_2SO_4$. Grams per liter.	κ_{20} observed.	Δ_{20}.
15.0	0.01965	86.5
20.0	0.02600	85.6
25.0	0.03140	82.9
30.0	0.03651	80.3
33.0	0.03950	79.0
35.0	0.04150	78.3

The conductivity found for the mixtures is seen to be considerably below the sum of the conductivities observed separately. The same is true for the next mixtures containing sodium chloride and phosphate. Here the same chloride solution was employed containing 18 grams to 500 cc., the dilution, by mixing, giving therefore always resultant products with 1.8 gram to 100 cc., or 18 grams to the liter. The phosphate solution was made with 20 grams of the ordinary salt, $HNa_2PO_4.12H_2O$, twice purified by crystallization, dissolved to make 500 cc. The volumes of this taken gave finally in the mixtures made 2, 4, 6, 8 grams, and so on, to the liter. Some stronger phosphate solutions were also investigated as the data were needed for certain reductions to follow. These figures are not given in the Kohlrausch tables quoted above.

TABLE II.—SODIUM CHLORIDE AND SODIUM PHOSPHATE.

NaCl solution = 20 grams to 500 cc.

$HNa_2PO_4.12H_2O$ solution = 18 grams to 500 cc.

$HNa_2PO_4.12H_2O$. solution. cc.	NaCl solution. cc.	Water. cc.	κ_{20} observed.	Δ_{20}.	Sum of conductivities.
5	..	95	0.000925	82.8	...
10	..	90	0.00175	78.3	....
15	..	85	0.00251	75.1	....
20	..	80	0.00323	72.4	....
25	..	75	0.00394	70.5	....
30	..	70	0.00462	68.9	....
40	..	60	0.00590	66.0	....
50	..	50	0.00720	64.4	....
5	50	45	0.02779	...	0.02824
10	50	40	0.02825	...	0.02906
15	50	35	0.02869	...	0.02982
20	50	30	0.02921	...	0.03054
25	50	25	0.02977	...	0.03125
30	50	20	0.03011	...	0.03193
40	50	10	0.03111	...	0.03321
50	50	0	0.03199	...	0.03451
..	50	50	0.027315	...	....

With the stronger phosphate solutions I found the following values:

TABLE II*a*.—SODIUM PHOSPHATE.

$HNa_2PO_4.12H_2O$. Grams per liter.	κ_{20} observed.	Δ_{20}.
25.0	0.00880	63.0
37.5	0.01245	59.4
50.0	0.01567	56.1
62.5	0.01868	53.5
75.0	0.02152	51.4
100.0	0.02650	47.4

Having found the effect of certain weights of urea, sodium phosphate and ammonium sulphate, mixtures were made containing the three substances at the same time with sodium chloride. Two solutions were used, one with 18 grams of the chloride to 500 cc., and the other with 9 grams of ammonium sulphate, 20 grams of sodium phosphate and 25 grams of urea to 500 cc. This in the table below is described as "mixture." Certain volumes of these solutions were then taken to make 100 cc. as shown in the tables, and the conductivities found.

TABLE III.—SODIUM CHLORIDE AND MIXTURE.

NaCl solution = 18 grams in 500 cc.

$$\left.\begin{matrix}(NH_4)_2SO_4\\ HNa_2PO_4.12H_2O\\ CON_2H_4\end{matrix}\right\}\text{mixture} = \left\{\begin{matrix}9\text{ grams in}\\ 20\text{ grams in}\\ 25\text{ grams in}\end{matrix}\right\}500\text{ cc.}$$

Mixture. cc.	NaCl Sol. cc.	Water. cc.	κ_{20}. observed.	Sum of conductivities, salt and mixture.	Sum of conductivities taken separately.
5	..	95	0.00234	....	....
10	..	90	0.00436	....	....
15	..	85	0.00622	....	....
20	..	80	0.00797	....	....
30	..	70	0.01136	....	....
40	..	60	0.01441	....	....
50	..	50	0.01733	....	....
5	50	45	0.02873	0.02965	0.02984
10	50	40	0.03031	0.03167	0.03209
15	50	35	0.03170	0.03353	....
20	50	30	0.03309	0.03528	0.03624
30	50	20	0.03559	0.03867	0.04003
40	50	10	0.03811	0.04172	0.04377
50	50	0	0.04052	0.04464	0.04726
..	50	50	0.027315	....	....

Expressed as grams per liter, the solutions finally used contained as follows:

Mixture. cc.	NaCl. Grams per liter.	$NH_4.SO_4$. Grams per liter.	$HNa_2PO_4.12H_2O$. Grams per liter.	CON_2H_4. Grams per liter.
5	18	0.9	2	2.5
10	18	1.8	4	5.0
15	18	2.7	6	7.5
20	18	3.6	8	10.0
30	18	5.4	12	15.5
40	18	7.2	16	20.0
50	18	9.0	20	25.0

In the last mixtures we have a complex case in which the conductivities of each of the four constituents are modified by the presence of all of the others. The resultant observed conductivities are the sums of the modified individual conductivities. It will be noticed that in the stronger mixtures the observed conductivities are about 10 per cent. lower than are the sums of the "mixture" and chloride conductivities taken alone. In the weaker mixtures, the discrepancies are naturally less. If we compare the observed values for the complete mixtures with the sums of the separate conductivities, the differences become very pronounced. For the strongest solution, the sum of the individual conductivities is over 15 per cent. greater than the value actually found for the mixture. This is in accord, of course, with what is well known about the conductivity of mixtures. The molecular or equivalent conductivity of a salt decreases with the number of molecules dissolved and this change follows in nearly the same proportion whatever the character of the salts, as long as they exhibit approximately the same dissociation and do not act on each other chemically. In expressing the conductivity of a mixture as made up of the sum of component conductivities, we can use a formula of this kind:

$$k = p_1\eta_1\Delta_1 + p_{11}\eta_{11}\Delta_{11} + p_{111}\eta_{111}\Delta_{111} + \text{etc.},$$

in which p_1, p_{11}, p_{111} are factors containing the effects of dissociation and viscosity in modifying the normal Δ values. Δ here represents the equivalent (or molecular) conductivity and η the concentration. In the case in hand, and probably for many similar cases, a simpler method of calculation leads to good results as the following will show. This is based on the assumption that in diminishing the conductivity of sodium chloride the addition of a relatively small amount of ammonium sulphate or sodium phosphate has the same effect as the addition of the same number

of sodium chloride molecules, and on this assumption I have calculated the modified conductivities in the following manner: If, using the Kohlrausch symbols, Δ is always the derived equivalent conductivity, κ any observed conductivity and η the corresponding concentration in gram-molecules per cubic centimeter, then we have:

$$\Delta = \frac{\kappa}{\eta};$$

or, if we take Δ from the tabulated results as known,

$$\kappa = \eta \Delta.$$

In the formula η corresponds to a given Δ, since Δ is calculated from a given η always. I have used the relation arbitrarily in a somewhat different way and have calculated κ from a given η and a Δ corresponding to a greater η. This use of Δ amounts, of course, to using a modifying factor, but a simple one. To illustrate, assume the following relation which I have found experimentally for two salt solutions:

Sol.	η.	Δ_{20}.
A or A_1	0.00005	99.92
B.....	0.00010	96.07

We may consider the second solution, B, as made up of two solutions, A and A_1 with $\eta = 0.00005$ for each. To find the conductivity of A in presence of A_1, we have, following the assumption referred to above,

$$\kappa = 0.00005 \times 96.07.$$

and for the conductivity of A_1 in presence of A, we have the same

$$\kappa = 0.00005 \times 96.07.$$

The sum of these gives the conductivity of B, or:

$$\kappa = 0.0001 \times 96.07 = 0.009607.$$

Consider in general two substances A and B in concentrations given below under η.

	η.	Δ.
Substance A,	C	P
	C + a	P_1
	C + b	P_{11}
	C + c	$P_{11'}$
Substance B,	R	p
	R_1	p_1
	R_{11}	p_{11}
	R_{111}	p_{111}
	R_m	p_m
	R_n	p_n
	R_o	p_o

a, b and c represent the equivalent concentrations R, R_1, R_{11}, ... expressed in terms of C, so that $C + a$ represents a concentration of substance A equal to the sum of $C + R$. The conductivity of substance A of concentration C in presence of substance B of concentration R is given by $\kappa = \eta \Delta = C P_1$. In presence of B of concentration R_1 we have $\kappa = C P_{11}$ and so on.

Next consider the conductivity of substance B in varying proportions in presence of A in concentration C. R_m expresses the concentration of the sum of the substances considered in terms of R and is, of course, equivalent to $C + a$. The equivalent conductivity of substance B of this concentration is not, however, P_1 but some other quantity as p_m. The conductivity of B in concentration R in presence of A in concentration C is therefore $R \times p_m$. In the same way $R_1 \times p_n$ expresses the conductivity of B in concentration R_1 in presence of C, and $R_{11} \times p_o$ the conductivity of R_{11} in presence of C. We have then for the total conductivity the sum of these modified conductivities, or,

$$\begin{array}{l} \kappa = CP_1 + Rp_m \\ \quad CP_{11} + R_1 p_n \\ \quad CP_{111} + R_{11} p_o, \\ \quad \cdots \quad \cdots \end{array}$$

while the simple sums of the conductivities would be

$$\begin{array}{l} CP + Rp \\ CP + R_1 p_1 \\ CP + R_{11} p_{11}. \\ \cdots \quad \cdots \end{array}$$

Similar relations will obtain for other mixtures of A and B.

In the following table are given the calculated conductivities of mixtures of sodium chloride and ammonium sulphate similar to those employed in the experiments recorded, the method of calculation being that just suggested. In the column headed "m sum" we have the values of C, $C + a$, $C + b$, etc., and under "Δ sum" we have the equivalent conductivities, P, P_1, P_{11}, etc.

TABLE IV.—CONDUCTIVITY OF NaCl IN PRESENCE OF $(NH_4)_2SO_4$.

NaCl. Grams per liter.	$(NH_4)_2SO_4$. Grams per liter.	Sum as NaCl.	m for NaCl. $m = 1000\,\eta$.	m for sum, $m = 1000\,\eta$.	Δ for sum as NaCl.	κ from η of NaCl and Δ of sum.
18	0.0	18.00	0.3077	0.3077	88.7	0.027315
18	0.9	18.80	....	0.3214	88.2	0.02714
18	1.8	19.60	....	0.3350	87.7	0.02698
18	3.6	21.19	....	0.3623	87.2	0.02683
18	5.4	22.79	....	0.3895	86.7	0.02668
18	7.2	24.38	....	0.4168	86.1	0.02650
18	9.0	25.95	....	0.4441	85.6	0.02634

Table V is analogous to the above, but gives the conductivities of the sulphate in presence of the chloride by the same method of calculation.

TABLE V.—CONDUCTIVITY OF $(NH_4)_2SO_4$ IN PRESENCE OF NaCl.

NaCl. Grams per liter.	$(NH_4)_2SO_4$. Grams per liter.	Sum as $(NH_4)_2SO_4$.	m for $(NH_4)_2SO_4$. $m=1000\,\eta$.	λm for sum. $m=1000\,\eta$.	Δ for sum as $(NH_4)_2SO_4$.	κ from η of $(NH_4)_2SO_4$ and Δ of sum.
0.0	0.9	0.90	0.013636	0.013636	117 6	0.001604
18	0.9	21.21	0.013636	0.3214	85.0	0.00116
18	1.8	22.11	0.02727	0.3350	84.5	0.00230
18	3.6	23.91	0.05454	0.3623	83.5	0.00455
18	5.4	25.71	0.08182	0.3895	82.6	0.00675
18	7.2	27.51	0.10909	0.4168	81.5	0.00888
18	9.0	29.31	0.13636	0.4441	80.6	0.01099

By adding the separate κ values, we obtain the values for the mixed solutions as calculated. These are shown in Table VI.

TABLE VI.—CALCULATED AND OBSERVED CONDUCTIVITIES OF MIXED NaCl AND $(NH_4)_2SO_4$.

NaCl. Grams per liter.	$(NH_4)_2SO_4$. Grams per liter.	κ calculated.	κ observed.	Difference.
18	0.9	0.02830	0.02839	0.00009
18	1.8	0.02928	0.02935	0.00007
18	3.6	0.03138	0.03151	0.00013
18	5.4	0.03343	0.03350	0.00007
18	7.2	0.03538	0.03560	0.00022
18	9.0	0.03733	0.03742	0.00009

The differences are very low and are within the limits of errors of experiment. Similar observations made with mixed chloride and phosphate solutions are given in the tables following:

TABLE VII.—CONDUCTIVITY OF NaCl IN PRESENCE OF HNa_2PO_4.

NaCl. Grams per liter.	$HNa_2PO_4.12H_2O$. Grams per liter.	Sum as NaCl.	m for NaCl. $m=1000\,\eta$.	m for sum. $m=1000\,\eta$.	Δ for sum as NaCl.	κ from η of NaCl and Δ of sum.
18	2	18.653	0.3077	0.3189	88.3	0.02717
18	4	19.307	....	0.3300	88.0	0.02708
18	6	19.961	....	0.3412	87.7	0.02698
18	8	20.614	....	0.3524	87.3	0.02686
18	10	21.268	....	0.3636	87.1	0.02680
18	12	21.922	....	0.3748	86.9	0.02674
18	16	23.229	....	0.3971	86.4	0.02659
18	20	24.536	....	0.4194	86.0	0.02646

TABLE VIII.—CONDUCTIVITY OF HNa_2PO_4 IN PRESENCE OF NaCl.

NaCl. Grams per liter.	$HNa_2PO_4.12H_2O$. Grams per liter.	Sum as $HNa_2PO_4.12H_2O$.	m for $HNa_2PO_4.12H_2O$. $m=1000\,\eta$.	m for sum. $m=1000\,\eta$.	Δ for sum as $HNa_2PO_4.12H_2O$.	κ from η of $HNa_2PO_4.12H_2O$. and Δ of sum.
18	2	57.08	0.01117	0.3189	54.6	0.00061
18	4	59.08	0.02235	0.3300	54.2	0.00121
18	6	61.08	0.03352	0.3412	53.8	0.00180
18	8	63.08	0.04469	0.3524	53.5	0.00239
18	10	65.08	0.05586	0.3636	53.1	0.00297
18	12	67.08	0.06704	0.3748	52.8	0.00354
18	16	71.08	0.08938	0.3971	52.1	0.00466
18	20	75.08	0.11173	0.4194	51.4	0.00574

TABLE IX.—CALCULATED AND OBSERVED CONDUCTIVITIES OF MIXED NaCl AND HNa_2PO_4.

NaCl. Grams per liter.	$HNa_2PO_4.12H_2O$. Grams per liter.	κ, sum calculated.	κ observed.	Difference.
18	2	0.02778	0.02771	0.00007
18	4	0.02829	0.02815	0.00014
18	6	0.02878	0.02812	0.00016
18	8	0.02925	0.02911	0.00014
18	10	0.02977	0.02967	0.00010
18	12	0.03028	0.03001	0.00027
18	16	0.03125	0.03101	0.00024
18	20	0.03220	0.03189	0.00031

The results given in the last table show a remarkably close agreement between the observed and calculated values. The variations are not greater than should be expected from calculations in which the Δ values are partly interpolated. In the next tabulation we have the combined effect of chloride, sulphate, phosphate and urea, the results being compared finally with those observed directly.

TABLE X.—EQUIVALENT CONDUCTIVITIES IN THE MIXTURES.

NaCl. Grams per liter.	$(NH_4)_2SO_4$. Grams per liter.	$HNa_2PO_4.12H_2O$. Grams per liter.	Sum as NaCl.	Sum as $(NH_4)_2SO_4$.	Sum as $HNa_2PO_4.12H_2O$.	Δ for total as NaCl.	Δ for total as $(NH_4)_2SO_4$.	Δ for total as $HNa_2PO_4.12H_2O$.
18	0.9	2	19.45	21.95	59.52	87.8	84.6	54.1
18	1.8	4	20.90	23.59	63.96	87.3	83.6	53.2
18	3.6	8	23.80	26.86	72.84	86.6	81.9	51.8
18	5.4	12	26.71	30.13	81.74	85.6	80.2	50.3
18	7.2	16	29.61	33.41	90.61	84.5	78.8	49.0
18	9.0	20	32.52	36.68	99.49	83.2	77.7	47.4

TABLE XI.—COMPARISON OF CALCULATED AND OBSERVED CONDUCTIVITES.

NaCl. Grams per liter.	$(NH_4)_2SO_4$. Grams per liter.	$HNa_2PO_4,12H_2O$. Grams per liter.	κ from η of NaCl and total Δ.	κ from η of $(NH_4)_2SO_4$ and total Δ.	κ from η of $HNa_2PO_4,12H_2O$ and total Δ.	Sum of κ values.	κ as found.	Difference. Calculated—found.
18	0.9	2	0.02702	0.00115	0.00060	0.02877	0.02873	0.00004
18	1.8	4	0.02686	0.00228	0.00119	0.03033	0.03031	0.00002
18	3.6	8	0.02665	0.00446	0.00232	0.03343	0.03309	0.00034
18	5.4	12	0.02634	0.00655	0.00337	0.03626	0.03559	0.00067
18	7.2	16	0.02600	0.00860	0.00438	0.03898	0.03811	0.00087
18	9.0	20	0.02560	0.01060	0.00530	0.04150	0.04052	0.00098

Here, as in the simple cases, the calculated conductivity is not far from the observed. For this mixture, the conductivities found are lower throughout than are the calculated values. But in the experiment made a certain amount of urea was present in each case and this, of course, lowers the conductivity. Assuming for calculation that the effect of this falls wholly on the sodium chloride, the following approximate corrections may be made, taking the mixtures in order.

TABLE XII.—FINAL CALCULATED CONDUCTIVITY.

No.	Sum of κ values.	Effect of urea.	κ corrected.	κ found.	Difference. Calculated—found.
1	0.02877	0.00005	0.02872	0.02873	—0.00001
2	0.03033	0.00009	0.03024	0.03031	—0.00007
3	0.03343	0.00019	0.03324	0.03308	+0.00015
4	0.03626	0.00028	0.03598	0.03559	+0.00039
5	0.03898	0.00038	0.03860	0.03811	+0.00049
6	0.04150	0.00047	0.04103	0.04052	+0.00051

It appears, therefore, that a very close approximation to the real conductivity of certain mixtures can be made by the method of calculation as suggested above, a closer approximation, in fact, than is given by some of the more complicated procedures which have been described.

As would naturally be expected, the departures from the observed values increase with the concentration of the solutions mixed. While the experiments were begun as a contribution to the question of the conductivity of urine, it is evident that the results obtained may find general application in cases where mixtures of moderate strength only are considered. The higher concentrations here are greater than are found in normal urine. The chlorine, calculated as sodium chloride, rarely reaches 18

grams per liter and the sulphate, calculated as ammonium sulphate, is usually below 4 grams per liter. The phosphoric acid of the urine as PO_4, is generally below 3 grams per liter, with the phosphate calculated as $HNa_2PO_4.12H_2O$, consequently below about 12 grams per liter. These amounts are therefore well within the weights of salts taken in the experiments. In addition the conductivity of the urine is rarely above 0.025 or 0.03 at most. From all this, taken in connection with the results of Table XI, it follows that with the salt of a urine known and the conductivity at 20° accurately determined, the conductivity of the non-chloride constituents may be found with a considerable degreee of certainty by diminishing by about 3 per cent. the chloride conductivity as calculated from tables for the given concentration, and subtracting this corrected salt conductivity from the observed urine conductivity. The remainder must give very nearly the true conductivity of the remaining substances in solution and must measure, in a manner, the amount of the electrolytes. The 3 per cent. correction for the chloride conductivity covers the average effect of the other salts present in normal urine. It is not to be supposed that the method would suffice to give a quantitative determination, but as an independent factor the non-chloride conductivity has a bearing and importance of its own, irrespective of the character of the salts which produce it.

NORTHWESTERN UNIVERSITY,
CHICAGO, November, 1903.

[FROM THE SHEFFIELD LABORATORY OF PHYSIOLOGICAL CHEMISTRY, YALE UNIVERSITY.]

THE DETERMINATION OF NITROGEN BY THE KJELDAHL METHOD.

BY ROBERT BANKS GIBSON.

Received November 11, 1903.

IN a recently published paper by Kutscher and Steudel,[1] the reliability of the Kjeldahl method for estimating nitrogen in various organic compounds of physiological-chemical importance has been called in question. These investigators have failed to obtain satisfactory results in the analysis of such substances as creatine, creatinine, uric acid, lysine and histidine by this widely

[1] Kutscher and Steudel: *Ztschr. physiol. Chem.*, **39**, 12 (1903).

used process; and they are thus naturally led to doubt the applicability of the Kjeldahl method to the determination of nitrogen in fluids and precipitates of animal (or vegetable) origin. The Kjeldahl method has become so useful in the prosecution of studies in metabolism, as well as in the direct analysis of a large variety of nitrogenous compounds that any criticism of its accuracy demands immediate consideration.

The Kjeldahl process is carried out differently in almost every laboratory. Kutscher and Steudel's method consisted in heating the substance (0.15-0.2 gram in the case of creatine) vigorously for about ten minutes with 10 cc. of concentrated sulphuric acid and a piece of copper sulphate; after cooling a little, potassium permanganate was added, the mixture again heated to boiling and then distilled in the customary manner. The results obtained in this way with creatine were extremely divergent and in nearly every case considerably below the theoretical values, the differences running as large as 7 per cent. There was, apparently, no fixed relationship between the discrepancies found and the duration of the boiling, or the quantities of copper sulphate and permanganate used. With creatinine from meat, the results were even more divergent. Although the data obtained from the analyses of uric acid show a closer correspondence with the theoretical requirements than in the preceding cases mentioned, yet the results varied from — 1.37 to + 0.67 per cent. Particularly noticeable is the failure to obtain duplicate analyses under identical conditions.

A critical examination of the protocols of Kutscher and Steudel shows that the period of heating employed by them—usually until the mixtures were clear—was considerably shorter than is customary with most analysts. In this country the use of permanganate has been abandoned almost entirely; in our own laboratory the Gunning modification[1] (with potassium sulphate) has been adopted for several years. The Gunning method was first officially studied in this country by the Association of Official Agricultural Chemists in 1891. It was adopted as an official alternative method in 1892 and since then has been used almost exclusively in the analysis of food products and fertilizers. It seeems to have been late in receiving recognition in physiological laboratories.

[1] Cf. Gunning: *Ztschr. anal. Chem.*, **28**, 188 (1889); Arnold and Wedemeyer: *Ibid.*, **31**, 525 (1892); Winton: *Ibid*, **32**, 478 (1893); *Chem. News*, **66**, 227.

The excellent results which we have obtained in the form of closely agreeing duplicate analyses in many hundreds of determinations on various materials (foods, urine, faeces, proteids, etc.) lead to the belief that the failure of Kutscher and Steudel is perhaps attributable to faulty technique rather than to an inadequacy of the Kjeldahl process in the cases studied. At Professor Mendel's suggestion I have, therefore, undertaken a considerable number of control analyses in which nitrogen was estimated in several typical physiological-chemical compounds, notably uric acid which is frequently determined by the Kjeldahl method and which Kutscher and Steudel failed to estimate with accuracy in this way. The inadequacy of the Kjeldahl-Gunning method in the case of a number of types of nitrogenous compounds is too well known to need consideration here. For creatine, creatinine and guanidine, the possibility of obtaining reliable results has lately been demonstrated anew by Beger, Fingerling and Morgen[1] and by Malfatti.[2] The latter in particular has called attention to the deficiencies and limitations in the use of permanganate to complete the oxidations. Extracts from our own protocols are given below. The decompositions were carried out with 20 cc. of sulphuric acid and 10 grams of potassium sulphate. The final titrations were made with N/5 or N/10 solutions. The length of time during which the flasks were heated (to boiling) varied considerably; the heating was, however, always continued for some time after the fluids first appeared colorless.

Uric Acid ($C_5H_4N_4O_3$).—The preparation (Kahlbaum's) used was recrystallized three times from concentrated sulphuric acid and dried at 105° C. The heated decomposing mixtures became colorless in from ten to thirty minutes. The heating was then continued over a hot flame for periods varying from forty-five minutes to two and one-half hours. For these titrations N/5 solutions were employed.

[1] Beger, Fingerling and Morgen: *Ztschr. physiol. Chem.*, **39**, 329 (1903).
[2] Malfatti: *Ibid.*, **39**, 467 (1903).

ANALYSES OF URIC ACID.

Quantity taken. Gram.	Nitrogen found. Gram.	Nitrogen found. Per cent.	Difference from theory. Per cent.	Duration of decomposition. Hours.
0.2140	0.07104	33.20	—0.18	1
0.1945	0.06482	33.33	—0.05	1
0.1945	0.06482	33.33	—0.05	1½
0.2081	0.06956	33.42	+0.04	1½
0.2061	0.06838	33.18	—0.20	2
0.2095	0.06985	33.34	—0.04	2
0.2464	0.08229	33.39	+0.01	3
0.6870	0.22940	33.39	+0.01	3
0.2807	0.09393	33.42	+0.04	2½
0.2992	0.09901	33.10	—0.28	2
0.2728	0.09072	33.26	—0.12	2½
0.2273	0.07637	33.58	+0.20	3
0.2739	0.09120	33.29	—0.09	3
	Average.....	33.33		
	Calculated	33.38		

Hippuric Acid ($C_9H_9NO_3$).—A well crystallized Kahlbaum preparation dried at 105° C. was used. The oxidizing mixtures became colorless in from one to one and one-half hours. The heating was continued for periods varying from one and one-half to three and one-half hours.

ANALYSES OF HIPPURIC ACID.

Quantity taken. Gram.	Nitrogen found. Gram.	Nitrogen found. Per cent.	Difference from theory. Per cent.	Duration of decomposition. Hours.
0.4794	0.03703	7.90	+0.06	3
0.3197	0.02488	7.78	—0.06	2½
0.9603	0.07518	7.82	—0.02	2½
0.7116	0.05535	7.78	—0.06	2½
0.6547	0.05076	7.76	—0.08	1½
0.5527	0.04387	7.93	+0.09	2
0.5293	0.04212	7.95	+0.11	3
0.6787	0.05298	7.80	—0.04	3½
	Average.....	7.84		
	Calculated	7.84		

Other Compounds.—A few analyses were made on preparations of leucine ($C_6H_{13}NO_2$), tyrosine ($C_9H_{11}NO_3$), urethane ($C_3H_7NO_2$), thiourea ($C_8H_{10}N_2S$), phenylmethyloxypyrimidine ($C_{11}H_{10}N_2O$) and *o*-aminobenzoic acid ($C_7H_7NO_2$), which have for the most part been recrystallized and dried at 105° C.

ANALYSES OF OTHER COMPOUNDS.

Substance.	Quantity taken. Gram.	Nitrogen found. Gram.	Nitrogen found. Per cent.	Nitrogen calculated. Per cent.	Difference. Per cent.
Tyrosine	0.3984	0.03137	7.87	7.76	+0.11
Tyrosine	0.3797	0.02990	7.87	....	+0.11
Leucine	0.3060	0.03256	10.53	10.70	—0.17
Urethane	0.5435	0.08614	15.84	15.76	+0.08
Urethane	0.3132	0.04973	15.87	....	+0.11
Thiourea[1]	0.4597	0.07813	16.68	16.86	—0.18
Phenylmethyloxypyrimidine	0.3814	0.05742	15.05	15.08	—0.03
Aminobenzoic acid	0.3145	0.03241	10.29	10.23	+0.06
Caseinogen	0.6362	0.09827	15.45	....	....
Caseinogen	0.4668	0.07223	15.49	....	....
Caseinogen	0.6109	0.09472	15.47	....	....
Caseinogen	0.4353	0.06736	15.47	...	....

The caseinogen used in the above analyses was a carefully purified preparation made according to Hammarsten's method. I. Munk[2] has already shown that the Kjeldahl method can be applied to give results comparable to those obtainable with the Dumas method with caseinogen, provided the heating of the decomposition mixtures is continued for a sufficiently long time. The figures here given indicate the possibility of obtaining comparable and reliable analyses even where the conditions are widely varied. In addition to these, reference may be made to a large number of determinations of the nitrogen content of various proteids carried out in our laboratory and also by Osborne[3] and his co-workers. In many cases these have been verified by the Dumas method.

The foregoing results afford no occasion to question the usefulness or accuracy of the Kjeldahl method as applied within a wide range of experimental conditions in the physiological-chemical laboratory. Indeed, it would be difficult to explain the numerous instances of duplicate analyses repeatedly made on the same substances, such as proteids, foods, etc., by different analysts under widely different conditions if the reactions involved were uncertain or variable in their character. When due care is exercised to procure a proper decomposition and oxidation of the

[1] When the decomposition mixtures obtained from thiourea were distilled while still straw-colored (and presumably incompletely oxidized), the results obtained were too low.

[2] I. Munk: *Archiv für Physiol.*, 1895, p. 551.

[3] Cf. various papers by Osborne in the Reports of the Connecticut Agricultural Experiment Station and This Journal, since 1892. Sadikoff has reported unfavorable results with some preparations of gelatins in *Ztschr. physiol. Chem.*, **39**, 411 (1903).

substances analyzed, uniformly satisfactory determinations can readily be obtained. For substances of unknown structure, however, the results furnished by the Kjeldahl process should not be accepted without verification by other methods.[1]

NOTES.

A Back Pressure Valve for Use with Filter Pumps.—The body of the valve is constructed of two pieces of glass tubing of fairly heavy gauge, drawn out as in sketch. The valve itself is an improvement on the old Bunsen valve, with a glass rod of slightly smaller diameter than the rubber tubing, wired on, to prevent collapse. Soft rubber tubing works best. The device has

given excellent service and can be made at little expense of time and material. It was originally devised for use with condensers in a laboratory where the water pressure sometimes gave out and the water ran back. It gives equally good service for both purposes.

R. N. KOFOID.

The Conversion of Calcium Oxalate to the Sulphate.—The customary process of reducing a calcium oxalate precipitate to a sulphate by applying a flame directly to a platinum crucible, after saturating the precipitate with sulphuric acid, is a slow one at best, and there is great danger of losing a portion of the contents of the crucible on account of boiling over or spattering.

These difficulties may be avoided by the following method: The precipitate is placed into a platinum crucible and saturated with concentrated sulphuric acid in the usual manner. A porcelain crucible about one-half inch larger in diameter than the platinum crucible is then filled about half full with powdered asbestos, or calcium sulphate, and the platinum crucible is sunk into the asbestos until it clears the porcelain crucible by about one-fourth inch at the bottom. After covering the platinum crucible loosely,

[1] Since the above was written, an article by Sörensen and Pedersen (*Ztschr. physiol. Chem.*, **39**, 513 (1903)) has appeared with reference to Kutscher and Steudel's work. For a further criticism cf. also Schöndorff: *Arch. f. d. ges. Physiol.*, **98**, 130 (1903).

the porcelain crucible is set in a pipe-stem triangle and placed over the full flame of a Bunsen lamp. The top portion of the platinum crucible is heated first and remains hotter than the bottom so that the excess of sulphuric acid boils out from the top of the precipitate, instead of from the bottom. The excess of acid is driven off in about one minute, the platinum crucible is then removed from the porcelain crucible and set over the flame until it is brought to a red heat. This method has been used successfully in over one hundred determinations of calcium.

ALFRED N. CLARK.

NEW BOOKS.

LABORATORY PHYSICS. A Student's Manual for Colleges and Scientific Schools. By DAYTON CLARENCE MILLER, D.Sc., Professor of Physics in Case School of Applied Science. Ginn and Co. 1903. 403 pp. Price, $2.15.

This laboratory manual, in the author's words, is meant "to be a student's hand-book for the performance of experimental problems in physics; the grade of work is that of the course in general physics in colleges and technical schools."

In Mechanics, we have general measurements, length, mass, time, acceleration, elasticity and density; under Sound, experimental problems are given in the measurement of the frequency of vibration, the velocity and wave-length of sound, etc.; under Expansion, thermometry and calorimetry. The subject of Heat Energy is considered, while a large part of the work is devoted to Light and Electricity. Under the former, photometry, mirrors and lenses, goniometry, index of refraction, wave-length of light, the interferometer and spectroscope are taken up.

The chapter on Electricity and Magnetism is probably the most important in the whole work. Resistance, current strength, electromotive force, capacity, induction and magnetic quantities are all studied at length.

The above synopsis will give a fair idea of the scope of this work. The book is written with unusual clearness, and the experiments are described in simple and concise language. The work will undoubtedly prove to be valuable to students of physics in the college stage of their work. HARRY C. JONES.

BLOXAM'S CHEMISTRY: Inorganic and Organic, with Experiments. 9th Edition, rewritten and revised by JOHN MILLAR THOMSEN, LL.D., F.R.S., Professor of Chemistry, King's College, and ARTHUR G. BLOXAM, F.I.C., Consulting Chemist and Chartered Patent Agent. Philadelphia: P. Blakiston's Son and Co. 1903. Price, $6.00.

All persons familiar with the earlier editions of this work will be delighted to renew acquaintance with an old friend in this revised form. It is refreshing to observe its mass of most interesting facts—real chemical information—such as the student truly needs to thoroughly comprehend, in his subsequent studies, the theoretical problems which may confront him. Due attention has been given the latest theoretical views and the basal principles of physical chemistry. They have not, however, been developed to the exclusion of all else. Some alterations have been made in the order of treatment of the non-metallic elements. Carbon now holds place after the three other typical elements—hydrogen, oxygen and nitrogen. Many of the old illustrations have also disappeared from the work. There is no division in the treatment of the fatty and aromatic bodies in the portion devoted to organic chemistry. The work is up to date. It cannot fail of a favorable reception, and will surely win new friends, which it deserves. E. F. S.

PHYSICAL CHEMISTRY IN THE SERVICE OF THE SCIENCES. BY JACOBUS H. VAN'T HOFF, Professor Ordinarius of the University of Berlin, Special Lecturer on Physical Chemistry. English version by ALEXANDER SMITH, of the Department of Chemistry in the University of Chicago. The Decennial Publications of the University of Chicago, Second Series, Vol. XVIII. 150 pp. Cloth, royal 8vo; net, $1.50; postpaid, $1.60. Chicago: The University of Chicago Press.

The eight lectures presented in this little volume have already appeared in German and been noted in this Journal, **24**, 1217 (1902). The volume before us, one of the decennial publications of the University of Chicago, is an unusually elegant one, which makes a strong appeal to the book lover as well as the chemist. From the fact, probably, that the lectures were originally given in English, this version reads more smoothly than does the German, and the former possesses a charm which one does not find in the latter. FRANK K. CAMERON.

LA CHIMIE PHYSIQUE, ET SES APPLICATIONS. Huit Leçons faites sur l'invitation de l'Universite de Chicago, par J. H. VAN'T HOFF. Ouvrage traduit l'allemand par A. CORVISY, Professeur agrège àu Lycée de Limoges. Paper, 78 pages. Paris: Libraire Scientifique A. Hermann, 6 et 12 rue de la Sorbonne. Price: 3.50 francs.

A French version of the van't Hoff lectures, based upon the German, already noted. The book is marred, however, by the use of the diagram on page 41, even though the German terms are translated in a footnote. The preparation of a new plate with French words would have involved but an inconsiderable expenditure and been much more satisfactory.

FRANK K. CAMERON.

THE CHEMICAL CHANGES AND PRODUCTS RESULTING FROM FERMENTATIONS. BY R. H. ADERS PLIMMER, D.Sc. (London). 184 pages. New York: Longmans, Green and Co. Price, 6 shillings.

This booklet is made up of interpretations and brief abstracts of the widely scattered contributions to this subject. Six chapters are devoted to fermentative changes in the carbohydrates, the field in which most investigation and research has been expended.

Proportionate space is given to the changes resulting in the formation of optically active products, the changes in fats and oils, uric acid, blood, milk and muscle. Three chapters are devoted to the more unusual varieties of chemical activity of which certain ferments are capable, *i. e.*, oxidation, reduction, nitrification, denitrification and synthesis.

The last four chapters deal with the cleavage of the albumin molecule as a result of the action of the digestive ferments pepsin and trypsin, and with the changes and products of the putrefaction of albumin. The selective action of particular types of microorganisms associated with putrefaction does not receive much attention.

The book contains a bibliography (32 pages), an author and a subject index. Diagramatic molecular formulas and equations are used freely. The German order of words is noticeable in a few sentences. The author's interpretation of the literature is fair and reliable. The book will be useful to students interested in the chemistry and physiology of fermentation.

ROB'T E. LYONS.

FERMENTATION ORGANISMS: A Laboratory Handbook. By ALB. KLÖCKER. Translated from the German by G. E. ALLEN and J. H. MILLAR. New York: Longmans, Green and Co. 1903. xx and 392 pp. Price, 12s. net.

The title of this book is misleading, since it does not deal with fermentations in general, but only with the alcoholic fermentations or those which influence the progress of the same.

The scope of the field covered is well stated by the author in his preface as follows: "The contents of the present work are divided into three sections. The first of these contains a description of the manner in which the science of the organisms of fermentation has gradually developed; at the same time an indication is given of the most important steps which have marked the progress of our science. The second section describes the fitting up of the laboratory and all that is necessary for conducting work. Laboratory methods are then explained, special attention being given to the preparation of pure yeast cultures in large quantities. Finally, the third section treats of the most important micro-organisms of the alcoholic fermentation industry. The book thus deals with that domain in which Hansen has opened up so many new paths."

The book is an excellent one and discusses the subject in clear and concise language. The translators, as well as the publishers, have taken great pains and have admirably succeeded in making the English translation very attractive.

Teachers and students of Technical Micro-biology, in the English speaking countries, will welcome this translation as an indispensable aid. Others working in allied lines, as in biology, bacteriology, pathology, hygiene and chemistry, will find in it much that is helpful and suggestive.

One of the most important features of the work is the very complete bibliography which occupies the last forty pages of the book. The bibliography embraces the titles of the most important researches and contains excellent explanatory notes.

W. D. FROST.

ELEMENTS OF INORGANIC CHEMISTRY. By HARRY C. JONES. The Macmillan Company, 1903. 242 pp.

A glance at the texts on general chemistry of the past fifteen or twenty years leads one to the conclusion that it is not an easy task for a writer to break away from the old order of things and to adopt the new. The discoveries and the developments along

various lines, and especially along the line of physical chemistry, have changed to a certain extent some of the fundamental principles of the science. Nothwithstanding this fact, few have ventured to embody these new theories in a general text, a majority preferring rather to hold to the older theories which have done such great service in the development of the science than to adopt the newer ones, even though they appear to harmonize more closely with the real facts.

Whether or not the time has come for the discarding of the old and the adoption of the new is an open question. It does seem certain, however, that if the science is to grow in the future, the newer theories must be recognized and embodied in our new text-books.

In the "Elements of Inorganic Chemistry," by Harry C. Jones, one finds the embodiment of both the old and the new. In addition to the older theories, the newer ones are taken up and briefly but clearly discussed. What was said in the preface of his larger work, "Principles of Inorganic Chemistry," concerning the aim of the book, applies also to the "Elements of Inorganic Chemistry." "The aim of the book is to add to the older generalizations those recently discovered, and to apply them to the phenomena of inorganic chemistry in such a way that they may form an integral part of the subject, at the same time, be intelligible to the student."

The general arrangement of the subject-matter is much the same as that found in a few of the best texts. The experimental work is well selected and follows each chapter. The book will, therefore, serve both as a text and a laboratory manual. The illustrations are familiar and quite numerous.

The most characteristic feature of the book is the brief, but exceptionally clear introduction to the new theories. More space has been given to these theories than will be found in any other general text yet published.

While the author evidently believes firmly that chemistry is to be a mathematical science, he nevertheless very wisely avoids using anything which is not within the understanding of the average student. The book seems simple enough for high-school text, and yet it is quite comprehensive enough for the average college.

G. B. FRANKFORTER.

CLINICAL EXAMINATION OF THE URINE AND URINARY DIAGNOSIS. A Clinical Guide for the Use of Practitioners and Students of Medicine and Surgery. By J. BERGEN OGDEN, M.D., Late Instructor in Chemistry, Harvard University Medical School; Assistant in Clinical Pathology, Boston City Hospital; Medical Chemist to the Carney Hospital; Visiting Chemist to the Long Island Hospital, Boston. Second edition, thoroughly revised. Philadelphia: W. B. Saunders and Co. 1903. 418 pp. Price, $3.00.

This work includes in its scope the methods for the detection and quantitative determination of the normal and abnormal constituents of human urine, the microscopic examination of urinary sediments, and the clinical diagnosis which may be made from the results of the examination.

The chemical as well as the microscopic methods are described in such detail that one who has had ordinary experience in chemical and microscopic manipulation may easily perform them. The entire ground of urinary analysis is well covered. The omission of the qualitative test for homogentisic acid (alkapton) to differentiate it from glucose in the copper tests for the latter is to be regretted. The method of determining the quantity of urea by Squibb's apparatus, which may be considered as a modification of the old Russell and West apparatus, might, with good reason, have been omitted on account of its furnishing results which are too high because of the incomplete absorpton of the carbon dioxide produced in the decomposition.

Notwithstanding that in the preparation of Fehling's solution (page 150) recommended by the author, the dilution of the solution with water is by an equal volume, one cannot be certain on boiling the solution that decomposition of the solution itself has not occurred. Greater dilution before boiling than that recommended is advisable, indeed, it is more prudent to dilute the Fehling's solution, as ordinarily prepared, with water to the extent of four times its volume before boiling. Thus it would be better to add about three volumes of water to the Fehling's solution, prepared as described by the author, so that it shall represent the customary Fehling's solution diluted with four volumes of water before boiling to prove its condition.

On the whole, the book is one of the best on the subject in the English language and is a credit to American urinary chemistry and diagnosis.

JOHN MARSHALL.